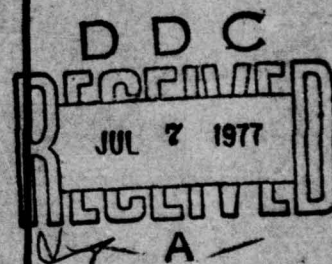


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12 TECHNICAL REPORT
TR-77-2-CEMEL

**RESEARCH ON COLORANT SYSTEMS
WHOSE CHARACTERISTICS MAY BE REVERSED:
PART II**



May 1976

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coordinates and luminous reflectance during forward and reverse reactions of the redox systems. Using two tin oxide electrodes, successful cells were found with anthraquinone-2,6- disulfonic acid (Na salt), an adjuvant and differently colored inert pigments. Attempts were made to apply the technique to textile-like materials with a combination called System 8 being the most promising. This system included nylon/stainless steel yarns and a redox system containing sodium sulfite, poly [N,N' (n-butylene)-4,4' bipyridylum dibromide] and N,N,N,N,-tetramethyl-P-phenylenediamine ditydrochloride. This combination produced an almost black color on the yarn in the forward reaction and became nearly colorless upon reversal.

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SUMMARY

This report describes continuation of the work begun under Contract DAAG17-73-C-0233 on redox systems whose spectral absorption and reflection characteristics can be varied reversibly by application of modest electrical potentials. Several anthraquinone derivatives have been investigated in cells consisting of at least one tin oxide transparent electrode, the other being tin oxide or some other selected metal. Cells were tested photometrically by reflection. For the compounds studied, the voltages needed were in the range up to 3.0 volts. To follow the color changes, cells were mounted on a Harrison-Shirley Digital Colorimeter, and both were determined during the forward and reverse reactions of redox systems contained in the cells. The color changes were referred to the CIE chromaticity diagram; lightness values were measured by the tristimulus value, Y. Measurements emphasized anthraquinone redox systems both with and without colored pigments being added. Employing two tin oxide transparent electrodes, successful cells were found with anthraquinone-2,6-disulfonic acid (disodium salt), and adjuvant and differently colored pigments. Experiments further suggested that cells could be operated with redox mixtures absorbed into a colored textile substrate sandwiched between electrodes. Cells containing mixed anthraquinone derivatives worked with one but not both compounds. Experiments were also carried out with 5,6-di-hydro-pyrazino-[1,2,3,4-lmn]-1,10 phenanthroline dibromide with different electrodes and adjuvants. Partial success was found, but during the course of experiments a self-energizing redox system was discovered. Some measurements were carried out to determine the potentials involved with such self-energizing cells. The final aim was to attempt application of redox systems to textile-like substrates, particularly by use of selected films. Films containing a viologen such as poly[N,N'(n-butylene)-4,4' bipyridylium dibromide] were found to be successful in a cell with a tin oxide transparent cathode and a silver/silver bromide anode. Some success was also found with films containing anthraquinone-2,6-disulfonic acid (disodium salt). Several other attempts were made to apply the techniques to textile-like material with particular success found for a combination called System 8. This system included nylon stainless steel yarns and a redox system consisting of sodium sulfite, poly[N,N'(n-butylene)-4,4' bipyridylium dibromide] and N,N,N',N'-tetramethyl-p-phenylenediamine dihydrochloride. This system produced an almost black color on the yarn on the forward reaction, and becomes nearly colorless upon reversal.

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PREFACE

This report describes the continuation of research begun under contract DAAG17-73-C-0233 and published as Technical Report No. 75-61-CEMEL. The objective was the exploration of various means of rapidly changing the spectral reflectance of a surface in a controllable manner. Successful approaches to such colorant systems could find application as adaptive camouflage whenever the color requirements varied from place to place. Certain approaches were excluded from this research because they had been the subject of earlier studies.

1. The photochromic approach was discarded because the color changes depended mostly on the uncontrolled intensity of solar illumination; the most effective colorants were highly toxic; the rate of reaction (basic sensitivity of the system) was inadequate; and the color changes produced often proceeded in an inappropriate direction.

2. Electrochromism (Stark effect) has never been demonstrated to produce color changes of interest to camouflage; theory predicts electric fields of 1 to 10 million volts per centimeter are required to produce even minimal changes in spectral absorption.

3. A liquid crystal approach has been investigated and appears to be plausible; it has yet to be reduced to practice. Ample knowledge exists as to the identity of suitable materials; the voltage (50 to 100 volts) requirements may appear excessive.

The purpose of the current research was to explore other colorant systems as alternatives to the liquid crystal approach, which functioned basically as an optical shutter. The present research explored oxidation-reduction reactions of colored substances, one of four approaches that were identified in the earlier contract. Factors that were emphasized were to

1. Devise a variety of chemical systems and determine the color changes in the forward and reverse directions in colorimetric terms,

2. Investigate the effects of mixing electrically sensitive colorants of different oxidation-reduction potentials to determine the feasibility of colorimetrically bi-model systems,

3. Investigate potential methods of application to flexible, fabric-like systems.

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RESEARCH ON COLORANT SYSTEMS WHOSE CHARACTERISTICS MAY BE REVERSED - PART II

1. Introduction

The work described in this report was guided by the same principle as used in the earlier work on colorant systems conducted under contract DAAG17-73-C-0233.¹ This principle was that any color can be produced to an observer at a distance by the correct additive processes carried out with areas of the three primary colors green, cyan (blue) and magenta (red), or for subtractive color processes with primaries of red, yellow and blue. Thus if a pattern of the colors can be displayed or masked by electrical methods, the colors necessary for the required camouflage can be changed at will. The actual pattern will depend on the pattern of electrical connections to the numerous cells making up the display.

In the previous work it was found from a survey of different methods to achieve the objective that the development of cells based on redox reactions offered the best solution to the problem. The cells that worked included the following: cells containing two inorganic redox systems together with a suitable indicator, cells containing diquaternary salts of bipyridyl-type compounds together with adjuvants and pigments, and cells containing colored anthraquinone derivatives that themselves had redox properties. A cell containing a diquaternary salt of bipyridyl-type compound together with adjuvant and pigment was successfully constructed and sent to US Army Natick Research and Development Command. Upon arrival, it was still found to function by the application of small potentials.

The first year of the contract demonstrated the feasibility of the approach. The contract was therefore extended to see whether these and any other redox systems could be developed sufficiently to be applied to textile substrates, or to substrates that could be substituted for textiles. If this could be achieved, the fundamental problem of camouflage with this type of system would be solved: the next problems would then be to construct the right pattern of colors and electrical connections necessary to vary these colors.

2. Anthraquinone Derivatives

a. Introduction

Near the conclusion of the work under the previous contract, it was discovered that anthraquinone-2,6-disulphonic acid (disodium salt) could be successfully used together with

¹Warwicker, J. D., Research on Colorant Systems Whose Characteristics May Be Reversed (Part I). Technical Report No. 75-61-CEMEL (CEMEL 138) June 1974.

potassium ferrocyanide to give color changes by electrical means. Since a range of colors could potentially be produced by anthraquinone derivatives, it was decided to explore this approach to the problem more extensively.

b. Cells Tested

Each redox system was tested in two ways: between two tin oxide transparent electrodes, and between a silver anode and a tin oxide transparent cathode.

System 1. 0.025*M* Anthraquinone-1,8-disulphonic acid (disodium salt)

0.025*M* Potassium ferrocyanide

1.0% Titanium dioxide

3.0% Agar

in water

System 2. 0.05*M* Anthraquinone-1,5-disulphonic acid (disodium salt)

0.025*M* Potassium ferrocyanide

1.0% Titanium dioxide

3.0% Agar

in water

System 3. 0.025*M* Anthraquinone-1-sulphonic acid (sodium salt)

0.025*M* Potassium ferrocyanide

1.0% Titanium dioxide

3.0% Agar

in water

System 4. 0.05*M* Anthraquinone-2-sulphonic acid (sodium salt)

0.025*M* Potassium ferrocyanide

1.0% Titanium dioxide

3.0% Agar

in water

c. Results of Tests

All these cells contained titanium dioxide so that they could be viewed by reflection and not be transmission, since this is more analogous to the final application. To test the cells, they were fastened to the aperture of the measuring apparatus so that they were illuminated by a light shining through the center of a selenium surface. The reflected light was thus registered on the selenium surface which was connected electrically to appropriate measuring circuits to register the current involved. Whilst so mounted, the cells had appropriate voltages applied and the percent reflectance measured via the selenium response. This was calibrated by substituting white or black surfaces for the cells. At the same time the current through the cells was also registered against time of application of the voltage. In a typical operation it is found that the light level falls from 100% reflectance (if calibrated against the original cell) to some lower value around 40% reflectance when the color has been developed in the cell. On reversal of the voltage, the reflectance again rises and, if an efficient reversal has been achieved, again reaches 100%.

System 1, with two tin oxide electrodes, on testing in this way, showed that the cell would operate at voltages up to 1.5 V but not at 2.0 V, when the light reflectance value failed to return to 100%. When a silver anode was employed with a transparent tin oxide cathode, the cell operated reversibly at voltages up to 2.0 V but not at 2.5 V.

System 2, with two tin oxide electrodes, showed that the cell operated up to 3.0 V, although very little advantage was gained between 2.0 and 3.0 V. When a silver anode was used with a transparent tin oxide cathode, the cell appeared to deteriorate progressively in performance on increasing the applied voltage from 1.0 to 3.0 V.

The data for system 3 with two tin oxide electrodes showed that the cell functioned reasonably well at applied voltages up to 3.0 V, whilst a similar cell employing a silver anode and a tin oxide transparent cathode functioned well at voltages of 0.9 to 1.3 V, but deterioration was shown at voltages of 1.4 and 1.5 V.

Only irregular results were obtained with system 4 with two tin oxide electrodes, but some improvements were found with a silver anode and a tin oxide cathode.

All the color changes involved with systems 1 to 4 were similar, namely, a pale yellow color changing to a red-brown color on application of the appropriate potential. The

results clearly show that the nature of the electrode plays an important part in the functioning of a cell, so that attention must be paid to the electrodes, if these systems are to be used in textile application.

3. Determination of the Chromaticity Coordinates of the Cells

a. Cells with Titanium Dioxide Pigment

Color can be specified by the tristimulus values X , Y , Z , of which the Y value is also a measure of lightness. The hue and saturation of the color are related to the relative magnitudes of X , Y , Z . To interpret the measured tristimulus values, it is useful to calculate the relative proportions of each by:

$$x = \frac{X}{X+Y+Z} \qquad y = \frac{Y}{X+Y+Z} \qquad z = \frac{Z}{X+Y+Z}$$

Since $x + y + z$ must equal unity, it is customary to specify only x and y ; known as the chromaticity coordinates of the color. If a diagram is constructed in which any point represents particular proportions of the tristimulus values and thus a specific color, this diagram is called the CIE Chromaticity Diagram.

It is convenient in defining both the colors for cells and the changes in color brought about by the application of potentials, to use the CIE system of chromaticity coordinates. The changes in chromaticity with voltage and time were determined using a large cell with a circular aperture of 4.0 cm. The two tin oxide transparent electrodes of the cell were separated by a circular spacer 2 mm thick. The actual values of chromaticity coordinate were determined by the use of the Harrison-Shirley Digital Colorimeter for systems 2 and 3, above. In every case the cell was driven forward for 1 minute before reversing the current for 2 minutes.

The chromaticity loops for system 2 indicate that the color change is initially towards orange, but then becomes redder especially at the higher voltages. On reversing the current, the return trace is similar to but not exactly the same as the forward trace. The trace does, however, return to the starting color. A plot of Y (tristimulus value) against time shows that the lightness of the cell decreases with time and increasing applied voltage.

System 3 also yields chromaticity data that show a color change towards red, the forward trace for different voltages following the same initial path. The reverse traces do not return along the same path, nor do they return to the exact starting color. However, as before, a plot of the Y against applied voltage shows that the lightness of the cell also decreases with time and applied voltage.

Further chromaticity data have been obtained for other anthraquinone systems in which the anthraquinone derivatives were reduced to a colored form. A background color was sometimes achieved by adding colored pigments to the cells, and an attempt was made to achieve a two-color effect by the use of two redox systems in the same cell with different redox potentials.

b. Cells Containing Colored Pigments

The system investigated was one with anthraquinone-2,6-disulphonic acid (disodium salt) with sodium sulphite and N,N,N,N-tetramethyl-p-phenylenediamine dihydrochloride as adjuvants. A combination of adjuvants had been shown previously to be successful. Chromatic pigments replaced the titanium dioxide. The cells were made from two tin-oxide transparent electrodes with the general contents as follows:

5%	Anthraquinone-2,6-disulphonic acid (disodium salt)
0.1%	Sodium sulphite
0.025%	N,N,N,N-tetramethyl-p-phenylenediamine dihydrochloride
3.0%	Agar

The Acramin pigments used were.

- (1) Acramin Yellow F7G
- (2) Acramin Green F3G
- (3) Acramin Blue FFG
- (4) Acramin Red FFG

The changes in chromaticity with voltage and time were followed for four cells, each with a different pigment. The current was reversed after 60 seconds; the results are shown in Figures 1 to 6 for the yellow pigment (1) included in the cell.

The traces for voltages 0.5, 1.0, 1.5, and 2.0 volts with the yellow pigment in the cell show an initial change to red, and on reversal of the polarity, the chromaticity traces returned approximately along the same path. On the reverse path, however, the trace went past the starting value of the chromaticity coordinates and became greener. This was presumably due to the oxidation of N,N,N,N-tetramethyl-p-phenylene diamine dihydrochloride at the electrode to give a bluish color. On switching off the current, this blue color disappeared and the cell returned to approximately the initial chromaticity coordinates. At higher applied voltages, 2.5 and 3.0 V, a more-or-less continuous loop was formed for the forward and reverse traces. The variation of Y with time and voltage is shown in Figure 7.

Similar data for the green pigment (2) are shown in Figures 8-14. For voltages of 0.5 and 1.0 V the color change was toward a brown color for the forward reaction.

For the reverse direction, the traces were similar to the above along the same path but overshooting to give a darker green color than the original, presumably owing to the same cause as discussed above. At the higher voltages of 1.5, 2.0, 2.5, and 3.0 V (Figures 10–13) approximately straight lines formed for both the forward and reverse reactions. The final chromaticity was virtually the same as the original. Figure 14 gives the variation of Y , the tristimulus value, with time and voltage.

Results for the cell incorporating the blue pigment (3) are shown in Figures 15–20. At all applied voltages, fairly smooth traces were produced, and on reversing the current, the traces returned along the same path, but again overshoot the original chromaticity coordinates. Changes in the tristimulus value, Y , are shown on Figure 21 for the cell with the blue pigment.

The chromaticity coordinate changes for the cell with red pigment (4) are only very slight. Figure 22 gives the trace for driving the cell at 3.0 V. Since the redox change is one to a red color, the red background tended to mask the changes involved. Variation in Y for the cell with red pigment, on Figure 23, however, showed that a reaction did indeed proceed, even though only a negligible chromaticity change was observed.

It is sometimes difficult to visualise chromaticity coordinates in terms of actual color. An aid to this is shown in Figure 24; Figures 25 and 26 summarise the findings just discussed for 0.5 and 3.0 V in the terms of the chromaticity diagram of the Commission Internationale de l'Eclairage (CIE). By a comparison of these charts it may be possible to have a clearer picture of the changes in color that were observed.

c. Experiments with a Fabric Scattering Matrix

A somewhat analogous system to those discussed above (inclusion of pigments in the cell) used a colored solid absorbent for the cell contents. As a preliminary to this work a yellow polyacrylic felt was used as the absorbent in the following cell:

Anthraquinone -2,7-disulphonic acid (disodium salt)	2.5%
Potassium ferrocyanide	5.0%
Agar	3.0%
Absorbed into yellow polyacrylic felt	
Electrodes: two transparent tin oxide electrodes	

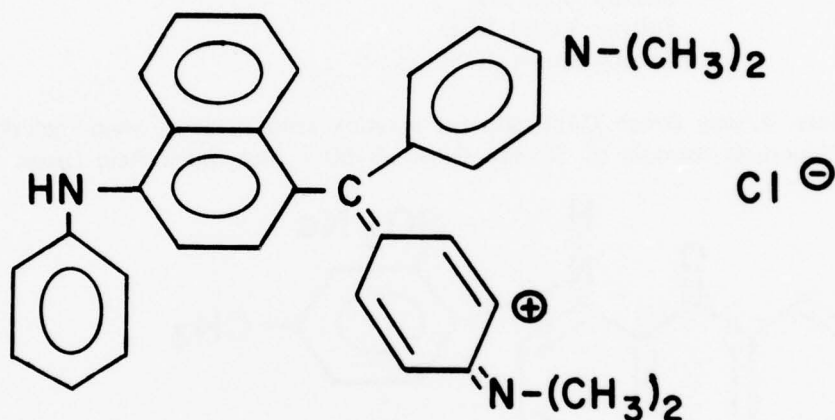
Chromaticity data were obtained at applied voltages of 2.0, 2.5 and 3.0 volts and are shown graphically on Figures 27 through 29. These traces indicate that the cell turned redder owing to the reaction of the anthraquinone salt. Reversal of the current eventually turned the color back to yellow and then on to green. The latter color, green arose from the oxidation of potassium ferrocyanide to potassium ferricyanide, a change to a blue color, which, in combination with the yellow felt, gave a green appearance. The variation of the tristimulus value, Y , with time and voltage is shown on Figure 30.

It is clear that cells of this type may be used as the basis for textile application, where combinations of the color of substrates with those of the cell contents at various voltages can give rise to a variety of controllable color changes.

d. Color Changes by Mixture of Two Redox Systems

The principle involved in these experiments was to mix two redox systems of different color ranges that could be changed at different potentials. Thus, by changing potentials over set ranges, the color of the system might change bidirectionally.

(1) The first attempt at a dual color change was the employment of anthraquinone-2,6-disulphonic acid (disodium salt) and Victoria Blue (a triarylmethane dye) in the same cell. Victoria Blue has the formula:



The composition of the cell was as follows:

- 0.1% Victoria Blue
- 5.0% Anthraquinone-2,6-disulphonic acid (disodium salt)
- 1.0% Titanium dioxide
- 3.0% Agar
- in water

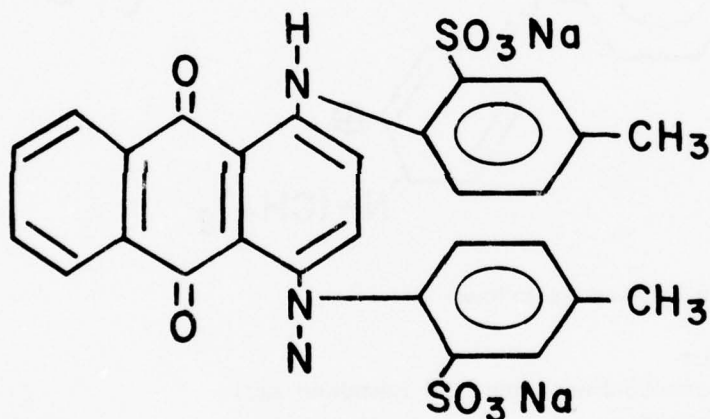
Electrodes: Silver Anode, tin oxide transparent cathode

(1) The titanium dioxide provided a white background against which color changes could be observed when measured in the Harrison-Shirley Digital Colorimeter. Chromaticity coordinates were measured against time and voltage. The reverse race was slightly different from the forward trace, but the cell did return nearly to the original set of chromaticity coordinates. It appeared that the Victoria Blue did not undergo a redox reaction at the transparent electrode but the anthraquinone salt did; hence, the reddish-brown color of the reduced anthraquinone salt was observed.

(2) Attempts were therefore made to find other anionic anthraquinone dye-stuffs to give different redox color changes. The dyes tested included the following:

Solway Celestol 200B
Solway Sky Blue BS
Coomassie Fast Grey 3GS
Carbalan Violet 2RS
Solway Blue BN
Solway Violet BRS
Solway Green G150

Of these, only Solway Green G150 showed a redox color change when included in a cell. The structural formula of Solway Green G150 (Color Index Acid Green 25) is:



It was included in a cell of the following composition:

0.2% Solway Green G150
5.0% Potassium ferrocyanide
1.0% Titanium dioxide
3.0% Agar

Electrodes: Silver anode and a transparent tin oxide cathode. The chromaticity traces are shown on Figures 31-34, and the variation of the tristimulus value of Y with time and voltage is shown on Figure 35. Since the essential color change was green to orange-brown, there was no advantage in mixing this dye with anthraquinone-2,6-disulphonic acid (disodium salt).

(3) Another cell with mixed dyestuffs was as follows:

Anthraquinone-2,6-disulphonic acid (disodium salt)	5.0%
Xylene Cyanol FF	0.1%
Titanium dioxide	1.0%
Agar	3.0%

Electrodes (a) Two tin oxide transparent electrodes
(b) Silver anode and tin oxide transparent cathode

With the two transparent electrodes (a) a color change from green to brown was observed with a voltage range of 2 to 3 volts: this is completely reversible but no dual color change was observed. With system (b), the same color change occurred but the color change started slowly on applying 1 volt, but the rate of color change increased at higher voltages. The reaction was completely reversible.

In this system, the anthraquinone derivative was apparently reduced to the red color, but with a green background provided by the Xylene Cyanol FF, the observed color was brown. The Xylene Cyanol FF itself, however, did not change color.

(4) Another cell containing a pair of dyestuffs was made up as follows:

Variamine Blue	0.05%
Disulphone Blue W	0.05%
Titanium dioxide	1.0%
Agar	3.0%
Tetrachlorohydroquinone	0.05%

Electrodes: (a) Two transparent tin oxide electrodes
(b) A silver anode and a tin oxide transparent cathode

Varying the voltage from 0.5 to 3.0 volts did not cause any measurable color changes.

(5) These experiments showed that with cells containing multiple dyestuffs, suitable mixtures have not yet been found with which to effect dual color changes. Experiments were therefore continued with mixtures of colored compounds that were not necessarily dyestuffs.

Poly[N,N'-(n-butylene)-4,4'-bipyridylium dibromide]	1.0%
Anthraquinone-2,6-disulfonic acid (disodium salt)	2.05%
	(0.05M)
Ammonium ferrous sulphate	1.96%
	(0.05M)
Agar	6.0%
Yellow pigment (Acramin Yellow FTG)	

Electrodes: two transparent tin oxide electrodes

The chromaticity traces for this cell are shown in Figures 36 and 37 for applied voltages of 2.5 and 3.0 volts, respectively. Both traces indicate that the cell went from green to blue and hence became darker (see Figure 38). Subsequent reversal of the current returned the cell virtually to its original chromaticity. It appeared both from the traces and also visually that the anthraquinone salt had no effect on the color change. This may be due to the rapid formation of the reduced dark blue color of the poly[N,N'-(n-butylene)-4,4'-bipyridylium dibromide] that effectively masked the red color that may have formed from the reduced form of the anthraquinone derivative. The cell is, therefore, not suitable for a dual color change.

(6) Another cell was made with two diquaternary salts as the main color changing components.

5,6-Dihydropyrazino [1,2,3,4-lmn]-1,10-phenanthroline	
dibromide	1.0%
Poly[N,N'-(n-butylene)-4,4'-bipyridylium dibromide]	2.5%
Agar	3.0%
Yellow pigment (Acramin Yellow FTG)	

Electrodes: silver/silver bromide anode and a transparent tin oxide cathode.

This cell was partly successful. On applying 0.5 V the cell turned orange-red at the cathode but did not reverse at this voltage or even on raising the voltage to 3.0 V for the reverse direction. On increasing the forward voltage to 1.5 V a blue-black color was formed, and with the residual red, the cell appeared black. On reversing the current at this voltage, the black color disappeared rapidly, but the red color remained.

Therefore, no satisfactory cell was discovered in which dual color changes were achieved by application of a range of voltages.

4. Preparation of Diquaternary Salts

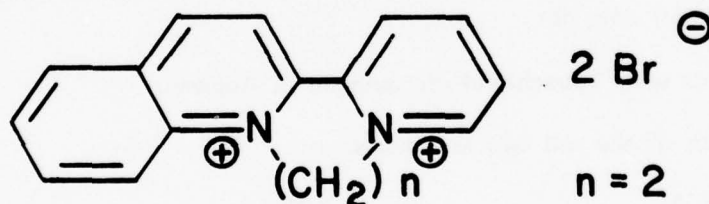
Since diquaternary salts were shown in the previous contract to have promise in systems, (see reference 1) a further investigation into this class of compounds was made to find the possibility of different color changes. Attempts, therefore, were made to prepare (I) 6,7-dihydropyrido [1'2':3,4] pyrazino [1,2-a] quinolinedi-ium dibromide and (II) 6,7-dihydropyrido [1'2':3,4] diazepino [1,2-a] quinolinedi-ium dibromide.

The compounds (I) and (II) require as starting material 2-(2-pyridyl)quinoline, and since this could not be obtained commercially, it had to be prepared.

a. Preparation of 2-(2-pyridyl)quinoline^{2,3}

First, 2-pyridyllithium was prepared by adding 7 ml of 2-bromopyridine to 30 ml n-butyllithium to form a dark brown precipitate. The reaction is violent and care is required. An ether solution of 2-pyridyllithium was added slowly to 9 g (0.07 Mole) of quinoline dissolved in 5 ml of ether to form a precipitate of 2-(2-pyridyl)quinoline. After the reaction was complete, the excess liquid was poured off and the precipitate was used immediately for the preparation of the diquaternary salts of 2-(2-pyridyl)quinoline.

b. Preparation of Compound I



The precipitate of 2-(2-pyridyl)quinoline, prepared as described above, was heated with 1,2-dibromoethane (20 ml) under reflux for 24 hours. The solution was allowed to cool, but no precipitate formed as expected, possibly because not sufficient 2-(2-pyridyl)quinoline had been produced in the first reaction.

²H. Gilman, W. A. Gregory and S. M. Spaty. J. Org. Chem. 16, 1788 (1951).

³For an alternative preparation see: A. P. Smirnoff, Helv. Chim. Acta. 4, 802 (1921).

According to Black & Summers⁴ a precipitate should have formed that could have been recrystallized from a mixture of ethanol and dilute aqueous hydrobromic acid to give yellow needles of a hemihydrate. This salt is said to give an olive-green color on reduction.

c. Preparation of Compound II

(Formula as above; $n = 3$)

The precipitate of 2-(2-pyridyl)quinoline was refluxed for 8 hours with 1,3-dibromopropane (20 ml) producing a tarry mass that could not be recrystallized. According to Black & Summers (ibid.) (see reference 4) the precipitate should be recrystallized from a mixture of ethanol and dilute aqueous hydrobromic acid to give yellow green crystals of monohydrate. This salt is said to give a brownish-green color on reduction.

Since a satisfactory preparation of neither of these compounds was achieved, their redox properties could not be determined.

5. Further Experiments with 5,6-Dihydropyrazino [1,2,3,4-Imn] -1,10-Phenanthroline Dibromide

This compound, for the purpose of this section, is labelled Compound A. It has been found that to prevent this compound from being reduced to a red color, the standard redox potential of the adjuvant must be greater than 0.612 V. Hydroquinone, with a standard redox potential of 0.612 V, does reduce compound A but tetrachlorohydroquinone ($E_0 = 0.664$ V) does not.

a. Experiments with Tetrachlorohydroquinone as Adjuvant

The composition of the cell was as follows:

Compound A	1.0%
Tetrachlorohydroquinone	1.0%
Agar	3.0%

Different electrodes were used for the different experiments.

⁴Black & Summers. J. Chem. Soc., 2771 (1971).

(1) Electrodes: stainless steel anode, transparent tin oxide cathode.

This cell started to function at 1.5 V, although the formation of the red color was slow. The color change was reversible at this voltage. Operational speeds increased as the voltage was raised (maximum applied voltage 3.0 V), and reversal was still found with the higher voltages.

(2) Electrodes: nickel anode, transparent tin-oxide cathode.

This cell operated up to 3.0 V with complete reversal; the speed was greater the higher the voltage. Care should be taken not to drive the cell forward for too long, since this leads to destruction of the transparent tin oxide electrode.

(3) Electrodes: gold anode, transparent tin-oxide cathode.

The cell operated satisfactorily in both directions at 2.0 V. No increase in speed was found for 3.0 V operation.

(4) Electrodes: Platinum anode, transparent tin-oxide cathode.

Only slight changes, which were reversible, were observed at 1.5 and 3.0 V.

(5) Electrodes: two tin-oxide transparent electrodes.

This cell did not work at all.

b. Ferrous Ammonium Sulphate as Adjuvant ($E_0 = 0.771$)

Composition of cell:

Compound A	1.0%
Ferrous Ammonium sulphate	1.0%
Agar	3.0%

(1) Electrodes: stainless steel anode, transparent tin-oxide cathode.

The cell functioned and reversed for voltages from 1.0 to 3.0 V, the speed increasing with voltage.

(2) Electrodes: nickel anode, transparent tin-oxide cathode.

The cell started to function and also reversed at 0.6 V. A much quicker reaction was obtained at 1.5 V, but the tin-oxide electrode was partly ruined.

(3) Electrodes: platinum anode, transparent tin-oxide cathode.

The cell worked slowly at 1.8 V with reversal: higher voltages did not greatly improve the speed.

(4) Electrodes: gold anode, transparent tin-oxide cathode.

Very slow changes at 2.5 and 3.0 V were observed, but they were reversible.

(5) Electrodes: two transparent tin-oxide electrodes.

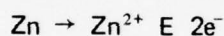
The cell started to function at 2.0 V and reversed slowly; no great improvement was observed at 2.5 and 3.0 V.

(6) Electrodes: Zinc anode and tin-oxide transparent cathode.

When the two electrodes were shorted, this cell functioned without an external additional voltage being applied; The resulting color was stable on open circuit. It required 6 to 9 volts to drive the cell back to its original state.

This system is, in effect, an electrochemical cell. On joining the two electrodes externally, Compound A plated out on the transparent tin oxide electrode in the reduced (i.e., red) form.

The reactions are:



(Ar^{2+} represents compound A)

This could form the basis of an automatic redox system, the color production being controlled by a variable resistance in the external link between the electrodes. Although it took 6 to 9 volts to drive the system back, the color faded when the electrodes were disconnected and also when the cell was exposed to air. Other systems based on this principle should be possible.

(7) Electrodes: copper anode, tin-oxide transparent cathode.

Color changes appeared slowly on application of 0.2 V. At 0.5 V the reaction was quicker, and the cell still reversed. The color change was rapid at 1.0 V, but complete reversal was not achieved, and some deterioration of the tin oxide electrode was observed. After operating at 1.5 V, which was extremely fast, no reversal was possible because the tin oxide electrode had been destroyed.

(8) Electrodes: Aluminum anode and tin oxide transparent cathode.

The aluminum itself affected the color change, even without shorting the electrodes.

These experiments are valuable because they show that it may be possible to build the power supply into the redox system and to produce effects without additional equipment, other than that required to do the necessary switching.

c. Self Energising Cells

The cells that change color spontaneously by shorting the electrodes are acting as primary cells. If they are to be incorporated into camouflage systems, it is necessary to know the electromotive force (emf) generated by them and their internal resistance. Consequently, some data were obtained with these cells to help in their assessment for use.

A circuit was set up in which the cell was placed in series with an ammeter and a resistor which could be varied in known steps. If E is the cell potential, i the current flowing, r the internal resistance of the cell, R_a that of the ammeter, and R the known variable resistance, then:

$$E = i (r + R + R_a)$$

$$\text{i.e., } R + R_a = E/i - r$$

By varying R and plotting $R + R_a$ (R_a was known) against the inverse of the measured current, i , the potential, E , of the cell was obtained from the slope of the line, and the internal resistance, r , from the intercept.

The cells consisted of a perforated zinc anode and a tin oxide transparent cathode separated by a spacer with a circular aperture. The thickness of the spacer and the diameter of the aperture were varied.

The redox system in the cell was 1.0% 5,6-dihydropyrazino [1,2,3,4-lmn]-1,10-phenanthroline dibromide with 1.0% tetrachlorohydroquinone as adjuvant in 3.0% aqueous agar gel.

TABLE 1. CELL DIMENSIONS

Cell	Diameter (mm)	Thickness (mm)
1	10.0	2.5
2	10.0	5.0
3	10.0	7.5
4	3.2	3.2
5	6.4	3.2

The readings obtained for the various cells are listed in Table 2.

TABLE 2. BASIC MEASUREMENTS OF CURRENT

Total External Resistance R+Ra	1/i (amperes ⁻¹)				
	Cell 1	2	3	4	5
200				4930	2130
300		1540		5780	2600
400		1790	1100	6670	2920
500	1640	2010	1790	7250	3280
600	1870	2230	2000	7810	3640
700	2080	2480	2180	8000	3950
800	2300	2680	2380	8130	4290
900	2530	2900	2560		4590
1000	2680	3130	2750		5000
1100	2900	3330	2960		5180
1200	3100	3530	3130		5320

With the external resistance values used, the measured current with cells 1, 2, and 3 were steady, and the values of E and r obtained were as follows:

TABLE 3. VALUES OF E, μ and ρ FOR THREE CELLS

Cell	E(volts)	μ (ohms)	ρ (ohm-cm)
1	0.483	304	955
2	0.452	408	640
3	0.521	437	458

With cells 4 and 5, the current did not attain a steady value but decayed continually. This may have resulted from the external resistance being too low in relation to the internal resistance of the cell, which caused excessive loading. Such factors as this must be taken into account, if these cells are to be considered.

6. Cells Employing Films

It was demonstrated above that redox systems can be set up whose spectral absorption and reflectance characteristics can be varied reversibly by the application of moderate electrical potentials. The next important step is to ensure that these reactions can be made to take place on a textile or similar substrate. One method of doing this is to incorporate the redox system into a film which then may change color on application of suitable potentials. Several such systems have been investigated.

a. Films Containing Viologens

As with other polycations, poly-bipyridilium compounds (polyviologens) readily form polysalts or polyelectrolyte complexes with polyanions. For example, solutions of polyxylylviologens form a precipitate with solutions of sodium polystyrene sulphonate or sodium polyacrylate. Such polyelectrolyte complexes are insoluble in common solvents but still retain their redox activity in solid form, as evidenced by immediate reduction with sodium hydrosulphite to produce violet or blue radical cations. Subsequent re-oxidation restores the original compound. This redox cycle is apparently repeatable indefinitely without any diminution of the effect.^{5,6}

b. Synthesis of Polyxylylviologen — Polyacrylate

The following types of sodium polyacrylate were used in the initial studies of polyelectrolytes to be complexed with poly[N,N'-(n-butylene)-4,4'-bipyridylium dibromide.

(1) Texigel* 23-004. Viscosity 1000 poise (25°C) pH: 10 to 11.5. An aqueous solution of a synthetic polyelectrolyte, mainly sodium polyacrylate.

(2) Texigel 23-005. Viscosity 400 to 800 poise. pH: 8 to 9. Mainly a sodium polyacrylate solution.

(3) Texigel 23-012. Viscosity 59 to 80 poise. pH: 6.5 to 7.5. Mainly a sodium polyacrylate solution.

⁵A. Factor & G. E. Hemsohn, *Polymer Letters* **9**, 289-293 (1971).

⁶A. S. Michaels, *Ind. Eng. Chem.*, **57**, No. 10, 32-40 (1965).

*Note: Texigel is a trade name of Scott Bader Company, Limited, Wellingborough, England

It is clear from the viscosity values that the chain lengths of these sodium polyacrylates are shorter successively; i.e., chain length $1 > 2 > 3$.

A polyelectrolyte was prepared by the addition of a 1.0% solution of poly[N,N'-(n-butylene)-4,4'-bipyridylium dibromide] in water to a 10% aqueous solution of the Texigel. Each Texigel was tried; all gave coarse precipitates of the polyxylylviologen-polyacrylate, but no apparent difference among the precipitates from the different Texigels was found. Such chain length differences will undoubtedly affect film-forming and other properties of the precipitates formed with these polyacrylates, but no differentiation of this nature was made.

The precipitates were dissolved in a solvent comprised of 60% water, 20% sodium bromide, and 20% acetone. Preparation of solutions of the precipitates, however, required prolonged shaking, at least overnight, with the solvent. Films were cast by pouring these solutions (the concentration of the solution was adjusted to give as good a film as possible) onto mercury, or into a petri dish. Upon evaporation of the acetone, a film formed which had a slight opacity. At this stage the film was washed very briefly with water and allowed to dry until the slight opacity again developed. The process was repeated three times to remove most of the sodium bromide; resultant film is then not easily soluble in water alone.

A water soluble film can be formed in a simpler way. The poly[N,N'-(n-butylene)-4,4'-bipyridylium dibromide] (solid) is mixed with the appropriate Texigel solution to form a viscous solution, which is then poured onto mercury and allowed to dry. Such a film sandwiched between a stainless steel anode and a transparent tin oxide cathode functioned reversibly at 1.0 to 1.5 volts to give a dark blue color at the cathode. It was found that a silver/silver bromide anode can be substituted for the stainless steel anode. Copper foil used as an anode failed to work unless about 6 to 9 volts were applied to the cell. The nature of the electrodes is again important, as has been found true in all the redox work described above.

c. Other Films

Films were made subsequently from two solutions

- (1) 0.25 Molar Potassium ferrocyanide
1.25% Texigel 23-005
- (2) 0.25 Molar Anthraquinone-2,6-disulphonic acid (disodium salt)
1.25% Texigel 23-005

These two solutions were degassed, and a layer of each was put on two separate tin-oxide electrodes. The layers were dried at 50 to 60°C to form two films, each attached

to a tin oxide electrode. One of the films was dampened and then pressed on top of the other film, thus forming a cell with two tin oxide transparent electrodes, making a sandwich of the two films. The electrode attached to the layer containing the anthraquinone salt was made the cathode, while the other electrode with the layer containing potassium ferrocyanide was made the anode. This cell worked satisfactorily at 2 to 3 volts, although its color was patchy. After standing two days, however, the cell ceased to function, because the film containing the potassium ferrocyanide had visible crystallized. Further work along these lines was carried out with the following solutions:

- (3) 2.5% Poly[N,N'-(n-butylene-4,4'-bipyridylum dibromide]
1.25% Texigel 23-005
- (4) 5.0% Ammonium ferrous sulphate
1.25% Texigel 23-005
- (5) 5.0% Tetrachlorohydroquinone
1.25% Texigel 23-005

Combinations used in the form of films as described above were:

films (3) + (4) and
films (3) + (5).

None of these cells worked at 3 volts. However, a single film of solution No. 3 between two tin oxide transparent electrodes went blue when 1.5 volts was applied, but the color could not be made to reverse. This again emphasises that the nature of the electrodes is important, since a similar cell but with different electrodes had previously worked.

d. Film of Polyviologen in Cellulose Acetate

The use of cellulose acetate in acetone with poly[N,N'-(n-butylene)-4,4'-bipyridylum dibromide] was not found to be successful in a cell with tin oxide transparent electrodes.

e. Films with Adjuvants

Experience with adjuvants incorporated into films showed that in time crystallization took place. As a substitute, it was though possible to cast a film of an organic resin in which oxidisable groups were incorporated which then could act as an adjuvant. A suitable organic resin seemed to be a phenol formaldehyde resin.

Hydroquinone (5.5 g) and 75% weight to weight basis of phenolsulphonic acid (10.96 g) were dissolved in 30 ml of absolute alcohol, to which 15 ml of 30% formaldehyde was added, and the whole kept at 60° for two hours, followed by one hour at 70°C. The resultant dark liquid was poured onto the conducting side of a transparent tin oxide electrode and heated at 80°C for one hour, which caused a brittle black film to be formed.

The resin itself did not appear to conduct electricity but was tested in a cell containing anthraquinone 2,6-disulphonic acid (disodium salt) between two transparent tin oxide electrodes. No current through the cell could be detected even when 3.0 volts were applied.

Thus, it seems that a conducting or semi-conducting polymer is required to act as an adjuvant, e.g., polyvinylhydroquinone or the semi-conductor formed between aromatic diamines and relatively strong acids, such as polyhaloquinones, e.g., tetrachloroquinone (chloranil)/p-phenylenediamine type complexes.

f. p-Phenylenediamine/Chloranil Semiconductor as Adjuvant

Equal volumes of hot saturated solutions of (1) p-phenylenediamine and (2) chloranil in benzene were mixed together, causing a black precipitate of the complex to form, which was filtered off, washed in ether, and dried.

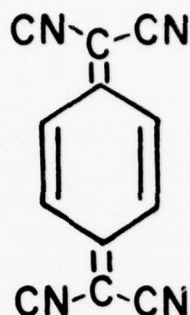
The complex was dissolved in acetone from which a film was formed. Such a film was found to be electrically conducting.

(1) A film of this complex was first deposited on the conducting surface of a tin oxide transparent electrode. A second film containing poly[N,N'-(n-butylene)-4,4'-bipyridylium dibromide] (1g) in Texigel 23-007 (10 g) was then deposited on top, and another tin-oxide transparent electrode completed the cell. Unfortunately, no color changes were observed with this cell, even up to applied voltages of 9.0 volts.

(2) A similar cell was made, but in this case the upper film consisted of anthraquinone-2,6-disulphonic acid (disodium salt) in Texigel 23-005 (10 g), but again no color changes were observed up to an applied voltage of 9.0 volts.

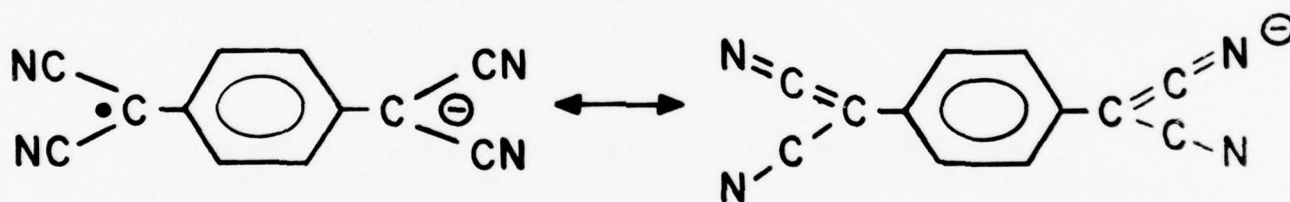
7. Conducting Salts of 7,7,8,8-Tetracyanoquinodimethan (TCNQ)

TCNQ has the structure:



According to W. R. Hertler, et al.,⁷ TCNQ is a strong II acid that forms three types of electrically conducting compounds, many of which are colored and with potential redox properties.

TCNQ forms crystalline π complexes (charge transfer complexes) with aromatic hydrocarbons, amines, and polyhydric phenols. These complexes have moderate resistivity (10^3 to 10^4 ohm-cm) and weak EPR absorption. In addition, TCNQ forms two series of stable, salt-like derivatives, each involving complete transfer of an electron to TCNQ with the formation of the anion-radical TCNQ $^{\cdot-}$ represented by the resonance hybrid.



The first series is represented by the simple salt formula $M^{+n}(\text{TCNQ}^{\cdot-})_n$ in which M may be a metallic or organic cation. These salts have moderate to high resistivity (10^4 to 10^{12} ohm/cm) and weak EPR absorption in the solid state. Members of the second of the salt-like series, i.e., the complex salts represented by the formula $M^{+n}(\text{TCNQ}^{\cdot-})(\text{TCNQ})_n$, contain a molecule of neutral TCNQ in addition to $\text{TCNQ}^{\cdot-}$; this series has exceptionally low electrical resistivity (10^{-2} to 10^3 ohm/cm) and variable EPR absorption.

⁷W. R. Hertler, et al., (J.A.C.S. 84 pp 3370-3393 (1962).

a. Preparations

A number of simple salts containing TCNQ were therefore prepared to see whether they could be used as suitable redox compounds in appropriate cells. When cast as films on glass slides, all these salts conducted electricity.

(1) $\text{Li}^+ \text{TCNQ}^-$

A boiling solution of 4.0 g (0.03 mole) of lithium iodide in 10 ml of acetonitrile was added to a solution of 2.04 g (0.01 mole) of TCNQ para-acetonitrile (distilled from phosphorus pentoxide) at the boil. Purple crystals separated from the dark brown solution on standing for four hours while still warm. These crystals were collected and washed on the filter with acetonitrile until the washings were bright green. Washing was then continued with a large volume of ether, after which the crystals were dried.

(2) $\text{Cu}^{++} (\text{TCNQ}^-)_2$

0.22 g $\text{Li}^+ (\text{TCNQ}^-)$ was dissolved in 20 ml of water and filtered. To this solution was added 1.2 g cupric sulphate in 7 ml of water. The greenish precipitate was dried in a vacuum desiccator over phosphorous pentoxide.

(3) $\text{Co}^{++} (\text{TCNQ}^-)_2 \cdot \text{H}_2\text{O}$

0.22 g $\text{Li}^+ (\text{TCNQ}^-)$ was dissolved in 20 ml of water and filtered. To this solution was added a solution of 0.8 g cobaltous sulphate in 7 ml of water. The blue-purple solid was filtered off, washed, and dried in a vacuum desiccator over phosphorous pentoxide.

(4) $\text{K}^+(\text{TCNQ}^-)$

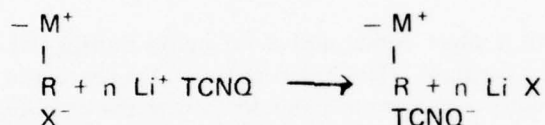
0.22 g $\text{Li}^+ (\text{TCNQ}^-)$ was dissolved in 20 ml of water and filtered. To this solution was added a solution of 0.8 g potassium iodide in 7 ml of water. The reddish-purple solid was filtered, washed, and dried over phosphorus pentoxide.

b. Films of TCNQ Salts

(1) 0.105 g $\text{Li}^+ \text{TCNQ}^-$ dissolved in 10 ml water was added to 0.123 g of poly[N,N'-(n-butylene)-4,4'-bipyridylium dibromide] (compound I) in 5 ml of water to form a dark blue precipitate. To this mixture was added 10 g of Texigel 23-004 and the whole thoroughly mixed. A further 0.25 g of compound I was added in the solid form and again the whole was thoroughly mixed. A film of the viscous mass was cast on mercury and allowed to dry at room temperature. The resultant dark blue film was found to conduct electricity when placed between two transparent electrodes, but did not show any color changes.

(2) 0.22 g of $\text{Li}^+ \text{TCNQ}^-$ in 15 ml water was added to 10 g Texigel 23-004 and mixed thoroughly. A solution containing 1.2 g cupric sulphate pentahydrate in 7 ml water was added and again the whole was mixed. However, on adding the copper sulphate solution the mixture went lumpy preventing thorough mixing. A blue colored film was cast on the lumpy mixture, but it was extremely brittle and did not appear to conduct electricity.

No films were made which incorporated the very highly electrically conducting complex salts of the type $\text{M}^n (\text{TCNQ}^-)_n (\text{TCNQ})$. However, J. H. Lupinski et al.,⁸ have prepared very highly electrically conducting polymers consisting of a polycation, 7,7,8,8-tetracyanoquinodimethan anions (TCNQ^-) and neutral TCNQ. The polycations employed were generally prepared by quaternization of a polymeric amine with an alkyl halide or sulphate. Since some of the redox compounds used in the present work were quaternized derivatives (e.g. poly[N,N'-(n-butylene)-4,4'-bipyridylium dibromide] and 5H-6,7-dihydro-1,4-diazepino (1,2,3,4-lmn)-1,10-phenanthroline dibromide), it was decided to react these compounds with $\text{Li}^+ \text{TCNQ}^-$ with a view to forming similar highly electrically conducting polymers. This reaction may be represented:



The polymeric TCNQ salt is formed as a precipitate when a quaternized polymer is treated with a solution (aqueous when $\text{Li}^+ \text{TCNQ}^-$ is used) of a TCNQ salt. Attempts to make such polymeric TCNQ salts were made as follows:

(3) The film in (1) above incorporated a polymeric TCNQ salt in Texigel 23-004, the polymeric salt was formed by reaction of 0.105 g $\text{Li}^+ \text{TCNQ}^-$ dissolved in 10 ml water, with 0.125 g poly[N,N'-(n-butylene)-4,4'-bipyridylium dibromide] dissolved in 5 ml water. In this case the polymeric precipitate formed was dark blue in color.

(4) When 0.105 g $\text{Li}^+ \text{TCNQ}^-$ in 10 ml of water was added to 0.125 g of 5,6-dihydropyrazino (1,2,3,4-lmn)-1,10-phenanthroline dibromide dissolved in 10 ml of water, a dark blue precipitate formed. This precipitate also conducted electricity.

(5) When 0.105 g $\text{Li}^+ \text{TCNQ}^-$ in 10 ml of water was added to 0.125 g of 5H-6,7-dihydro-1,4-diazepino (1,2,3,4-lmn)-1,10-phenanthroline dibromide dissolved in 10 ml of water, again a dark blue precipitate formed. This precipitate conducted electricity.

⁸J. H. Lupinski et al., Journal of Polymer Science: Part C, No. 16, pp 1561-1578 (1967)

In none of the above cases was a color change observed upon application of electrical potentials. Interest in the compounds stemmed from their high conductivity and their possible use as flexible electrode materials. Unfortunately, their deep blue color appears to preclude such use. Lupinski, (see reference 8) in their work on new classes of film-forming, electrically conducting polymers employed many different polycations. However, they made very few comments on the color of the polymeric TCNQ derivative formed. It may, however, be possible to find a polymeric TCNQ salt which is virtually colorless into which redox systems could be incorporated.

c. Color Changes of TCNQ

TCNQ in 50:50 acetone-water solutions can be shown to change color from a pale yellow-orange color to a green by the addition of zinc powder. It is apparently capable of redox color changes and, therefore, cells were made in which TCNQ provided the color change.

1.0 Tetracyanodimethan
5.0% Ferrous ammonium sulphate
In acetone-water (50:50) mixture

A cell was made up with a silver anode and a tin oxide transparent cathode with the above solution as the redox medium. The initial color of the cell was a milky yellow and on application of 1 to 3 volts a grass-green color formed at the cathode, which could be reversed. It was found, unfortunately, that on standing, the silver slowly reduced the TCNQ to the reduced green form.

The solution was then tried in a cell with (a) a platinum anode with a transparent tin oxide cathode and (b) a gold anode with a transparent tin oxide cathode. Both cells worked satisfactorily at voltages of 1 to 3 volts. On standing, neither cell showed any reduction by the platinum or the gold anodes.

Note: The addition of ferrous ammonium sulphate ($E_0 = 0.771V$) to TCNQ solution tended to turn the solution slightly green. Tetrachlorohydroquinone ($E_0 = 0.664V$) added to TCNQ solution turned it completely green. Therefore, it seems that a suitable adjuvant must have a value of $E_0 > 0.771V$.

8. Miscellaneous Color Reactions

a. The following solution was tested for redox properties between two electrodes separated by a glass spacer.

0.1M, Ferrocene
0.1M, 1,2-Naphthoquinone-4-sulphonic acid (sodium salt)

These compounds were made up in a 50:50 DMF water solution.

The electrodes employed were as follows:

- (1) a silver anode and a transparent tin-oxide cathode.
- (2) two transparent tin-oxide electrodes.

In neither (1) nor (2) was a color change found at the anode, but a color change was found at the cathode when a voltage of 2.0 to 3.0 volts was applied. This color change was an orange to a dark red, and could be reversed by application of reverse voltage. 1,2-Naphthoquinone-4 sulphonic acid is therefore another possible redox compound.

b. Many dyes in the acid and disperse classes of dyestuffs are anthraquinone derivatives that can be made to change color by chemical reduction. A number of these dyes were therefore selected and tested, first by chemical methods to ascertain whether a color change was possible, then electrical reduction was attempted in a redox system.

The dyes tested were:

Cibacet Blue 2R	Cibacet Brilliant Pink 4BN
Cibacet Brilliant Blue BG	Carbolan Blue B
Carbolan Violet 2RS	Alizarin Light Blue 2GL
Polar Brilliant Blue RAW	Solway Sky Blue BS
Coomassie Fast Grey 3GS	Duranol Brilliant Yellow 6G
Duranol Red 2B	Duranol Red X3B
Duranol Violet 2R	Duranol Brilliant Violet B
Duranol Brilliant Violet BR	Duranol Blue G
Duranol Blue 2G	Duranol Brilliant Blue G

All of these dyes were reduced to a different color by chemical methods, but none could be reduced in redox systems up to a maximum applied voltage of 3 volts.

9. Application of Redox Systems to Textiles

The work that has been described has largely been carried out in cells, since the main objective was to find suitable redox colorant materials. However, the long-range objective of the research is to construct a camouflage system that can be changed by electrical means. Such a system must of necessity be on a flexible substrate and, in general, must be applicable to textiles, which can be made into garments, covers, or other articles that require camouflage.

The problem, therefore, becomes one of translating the information gained by the use of cells into a form that can be used in textile systems. It is, of course, theoretically possible to make up a garment in flexible cells, by the use of transparent flexible sheeting suitably divided into such cells like a quilt. The difficulties with such a scheme lie in making the flexible plastic material conducting, and also in the sensitivity of an item made from such material to extraneous damage that could destroy its effective use.

These problems were thought best solved by the use of redox systems incorporated into textile yarns, which could by some process be made conducting. However, many problems are involved in this approach because redox systems that operate perfectly satisfactorily in the rigid cells described above may not operate at all under textile-like conditions. Thus, not only is a textile system to be constructed, but modifications may be required for successful redox systems to be applied.

Only a start has been made on this problem, but results show that there is a possibility that the problem can be solved satisfactorily.

a. Preparation of an Electroconductive Filament

According to Japanese Patent 73,⁹ conducting, durable, flexible polyester fibres were manufactured by depositing an electroconductive coating of metal particles in polyester polyurethane containing polyester segments identical with the structure of the fibre.

To produce these filaments, a 15-denier polyethylene terephthalate fibre was coated with a paste containing 85 parts silver microflakes and 100 parts of a 15% diphenylmethane diisocyanate ethylene glycol pentaerythritol terephthalic acid polymer (in m-cresol). This polymer was obtained by dissolving 100 parts poly (ethylene terephthalate) containing 0.8 mole percent pentaerythritol in 700 parts dimethylsulphoxide at 160°C under nitrogen, adding 17.6 parts of ethylene glycol and 824 parts dimethylemethane diisocyanate, precipitating in water, filtering off, washing and drying. The 2.8-micrometer-thick coating was dried for 6 seconds at 190°C and 6 seconds at 240°C to produce a fibre with an electrical resistance of 40 ohms/cm tensile strength 2.5 g/denier with an elongation at break of 24%, without sacrificing softness or flexibility.

An attempt to follow this procedure was partially successful, the silver appearing in patches on the treated Terylene fibre. However, when the paste was applied from a more dilute m-cresol dispersion an electrically conducting fibre with no surface agglomeration of silver was produced. This method therefore offers a possible way of introducing conducting leads in textile fabrics without recourse to wires, but no further work was done on this problem at this stage.

⁹Japanese Patent 73, 38040 Through Chemical Abstracts 83 61405W (1975).

b. Experiments with Stainless Steel -- Nylon Yarns

The Bekitex H yarn (Registered Trade Name) used in these experiments contained 75% nylon 66 and 25% of stainless steel fibres. It is conductive and is normally used in static control in textiles. For the purposes of camouflage it offers advantages as a dyeable, conductive yarn.

To test the use of Bekitex H yarn in a redox system, a wire was first braided with viscose rayon and then with Bekitex H yarn in a pickmaster braiding machine. This unit was then sealed into a glass tube as shown in Figure 39, but at the start of the experiment one end was left open to allow the necessary reagents to be inserted. Before inserting into the tube it was found advisable to wet the yarn out first, fill the cell and then seal the tube with quick-setting epoxy resin.

The metal of the central wire anode could be varied but it was usually either stainless steel, gold, or silver. Better results were obtained with silver than with stainless steel.

In filling the cell, the redox solution was introduced and the yarn and solution degassed under vacuum before the open end of the tube was finally sealed off.

Several redox solutions were tried in such cells as follows:

- (1) 2.5% Anthraquinone -- 2,6-disulphonic acid (disodium salt)
1.0% Potassium ferrocyanide
Bekitex yarn cathode, stainless steel anode
Applied voltage 2.5 volts

The red color was slow to form on the cathode (about 3 to 4 minutes) but disappeared a little quicker on reversing the current (about 2 minutes). Application of a higher voltage (3 volts) resulted in gassing.

Gelled solutions were tried to keep the color change near to the electrodes.

- (2) 2.5% Anthraquinone -2,6-disulphonic acid (disodium salt)
1.0% Tetrachlorohydroquinone
6.0% Gelatin

This cell failed to function even on the application of 3.0 volts.

- (3) 5.0% Poly[N,N'-(n-butylene)-4,4'-bipyridylium dibromide]
1.0% Tetrachlorohydroquinone
3.0% Agar

The solution was gelled on to the fibre in the tube by a quick cooling in ice; a dark-grey gel was formed. On application of 1.5 volts the yarn went blue very quickly, but the cell would not reverse even when 3 volts was applied.

(4,5) A variant on the above systems used (4) silver and (5) nickel wire anodes with the solutions:

2.0% 5,6-Dihydropyrazino (1,2,3,4-lmn)-1,10 phenanthroline
dibromide
2.0% Ammonium ferrous sulphate

(6) For comparison a stainless steel anode was also used.

In the cells 4, 5, and 6 a red color formed on the Bekitex yarn on application of 0.5 volts, but it could not be reversed even by the use of 3.0 volts.

On further investigation, it was found that owing to the Bekitex yarn being too closely braided, the reduced form of the redox compound was formed on the inside of the braiding with little being visible on the outside. Current density is also a factor, since the surface area of the central wire anode is small, whereas the surface area of the Bekitex Braided yarn is considerably larger.

(7) Figure 40 shows a variation of the cell design. When a solution of

2.5% Anthraquinone-2,6-disulphonic acid (disodium salt)
5.0% Potassium ferrocyanide

was placed in the cell and voltage up to 3.0 volts applied, very little color formation was observed on the cathode in the spaces in the spiral at the higher voltages (2.5 to 3.0 volts), whereas none at all was formed at voltages below 2.5 volts.

The above solution, when tested in a cell as shown on Figure 39, with (a) a gold wire anode, and (b) with a carbon fibre anode, produced a good color change, but it functioned only for one cycle. Application of voltages of greater than 2.5 volts produced evolution of gas at the electrodes.

In the design of such tubular cells, it was found that for optimum performance, the Bekitex yarn had to be braided in an open manner. On the other hand, it was found necessary to closely braid the inner viscose layer to prevent possible short circuiting of the cell.

(8) A particularly good system was found with a cell of the design shown in Figure 39. The anode was a silver wire and the cathode was an open-braided Bekitex yarn. The cell was filled with the following solution.

5.0% Poly[N,N'-(n-butylene)-4,4'-bipyridylium dibromide]
2.5% Sodium Sulphite
0.6% N,N,N',N'-Tetramethyl-p phenylenediamine dihydrochloride

This system produced extremely rapid color changes in both forward and reverse directions. However the system was always reproduced; and the cause of the occasional failure has not yet been discovered.

c. Potential Use

System 8, when working correctly, gives a dark color on application of the voltage (up to 1.5 volts) and is virtually colorless when reversed. As pointed out above, if the cell is properly constructed, it works well with multiple cycles; but occasionally cells are constructed that do not work or work only very sluggishly for unknown reasons. This is the main problem with this cell and, if this can be solved, this system offers a lead into the textile camouflage application. It will be appreciated that the Bekitex yarn is 75% nylon 66 which is capable of being dyed any desired color. If, therefore, a colored Bekitex yarn can be used in the cell, then the intent of the redox action is to mask the color on application of the voltage, and reveal the base color on reversal. The germ of a textile camouflage system that can be electrically controlled appears to lie within the system last described above.

There are problems still to be solved beside the one mentioned above. It is clearly impossible to envisage a viable camouflage system with glass surrounding the textile and containing liquid. If the liquid can be made to gel and be absorbed by the textile, the problem reduces to one of keeping the system damp enough for the redox change to take place. It is conceivable that this can be solved at least partially by a thin transparent polymer coating over the textile system.

On the other hand if a color-changing polymer can be incorporated into the Bekitex yarn, then little liquid would be required. The yarn itself can be differently constructed; thus instead of nylon, cotton could be substituted, and this alone may retain enough moisture (or be modified to retain moisture) to allow the system to work.

Several ideas have been mooted, such as a nonwoven fabric base with silver sputtered on one side to form an anode and laid on a weave of Bekitex yarn that forms the cathode. This could be sandwiched together with a thin transparent polymer cover, so that with suitable connections, the correct redox solution and dyed areas would form a camouflage cloth.

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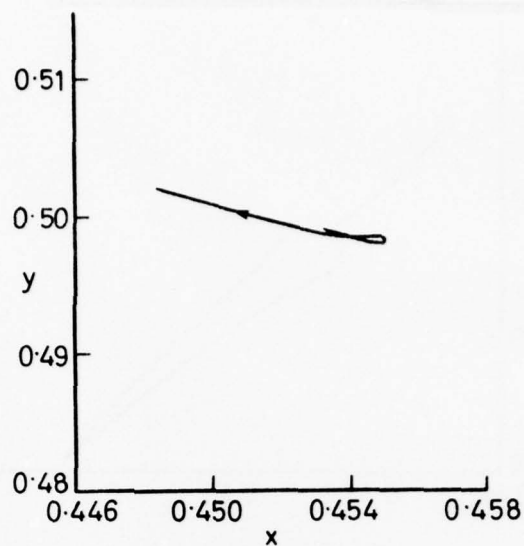


Figure 1. Yellow Pigment, 0.5 volt.

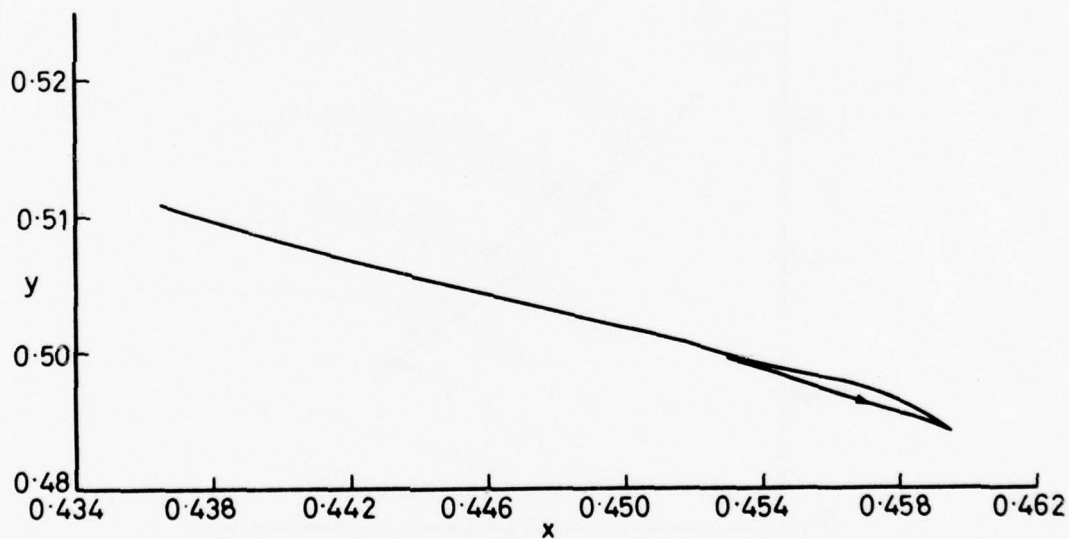


Figure 2. Yellow Pigment, 1.0 volt.

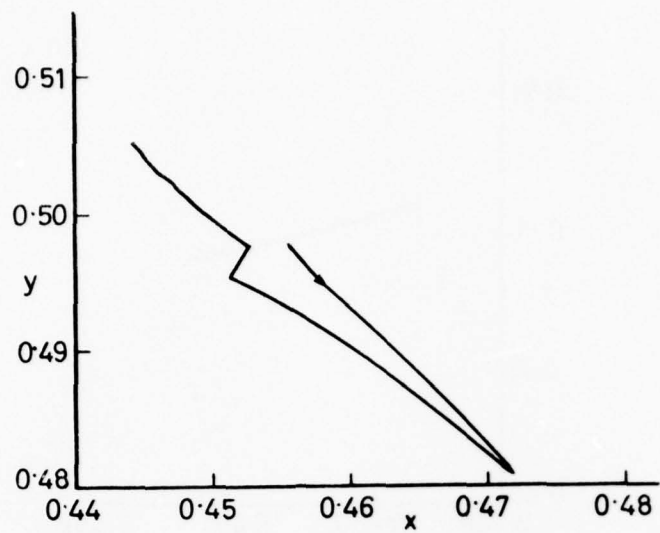


Figure 3. Yellow Pigment, 1.5 volts.

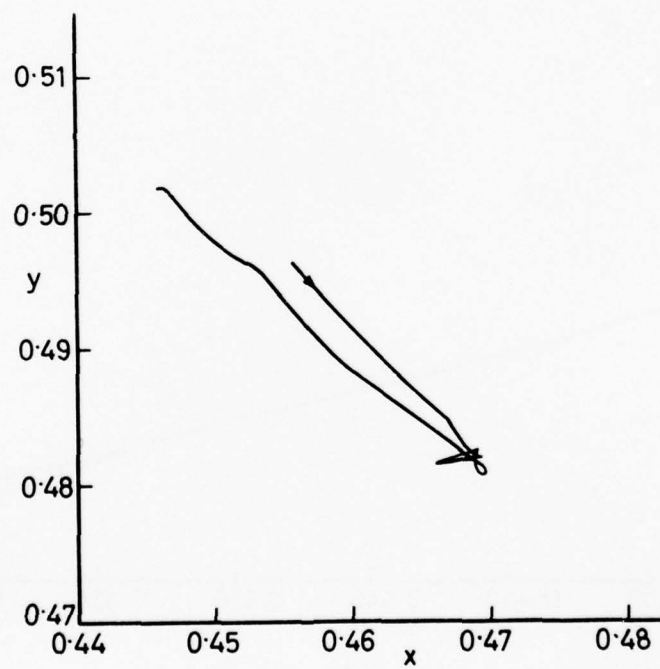


Figure 4. Yellow Pigment, 2.0 volts.

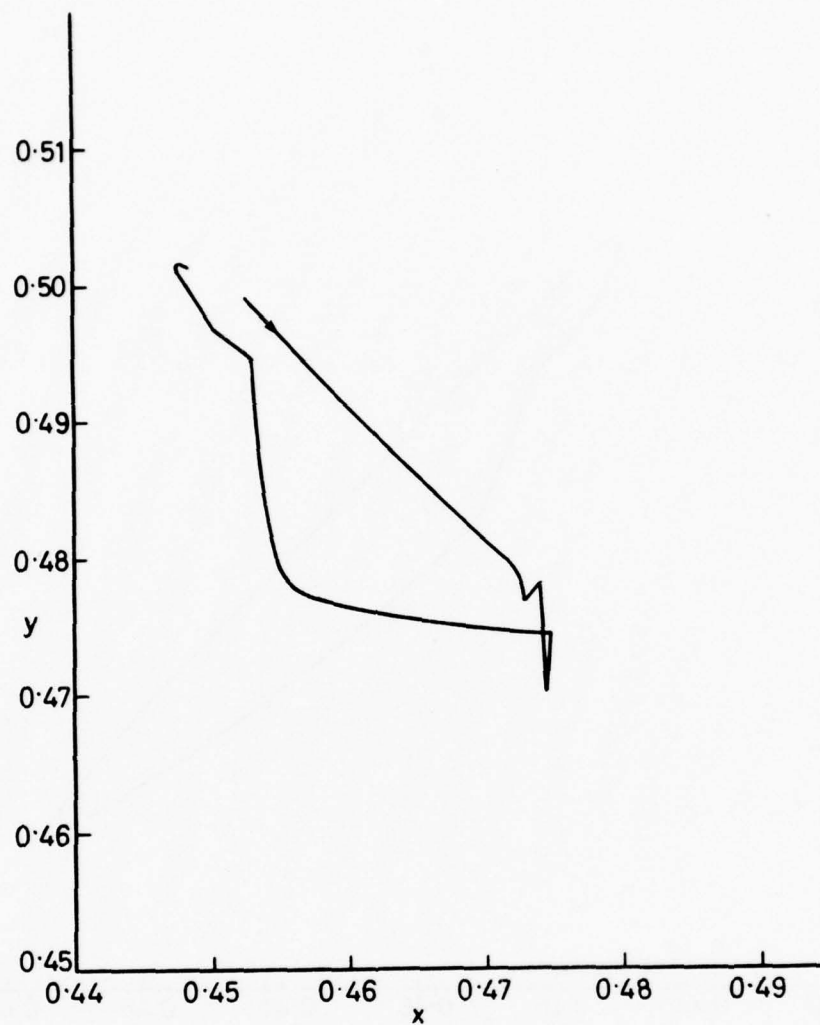


Figure 5. Yellow Pigment, 2.5 volts.

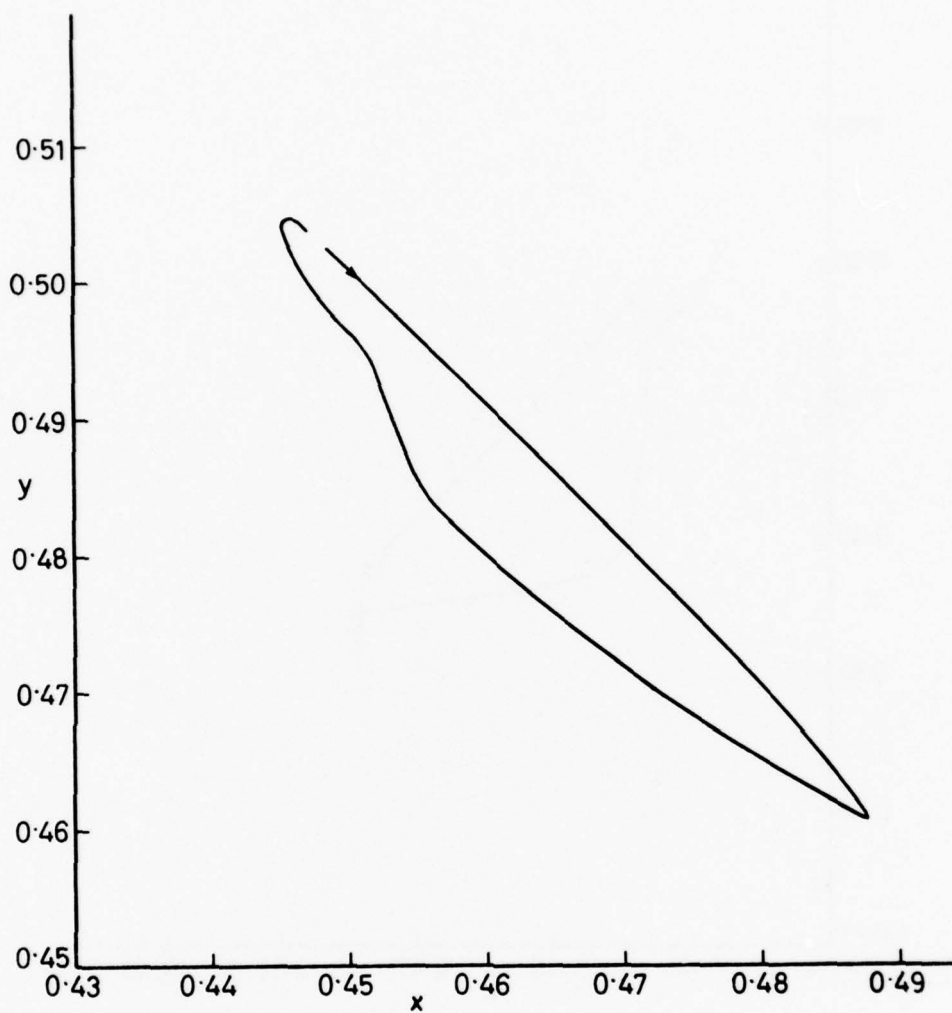


Figure 6. Yellow Pigment, 3.0 volts.

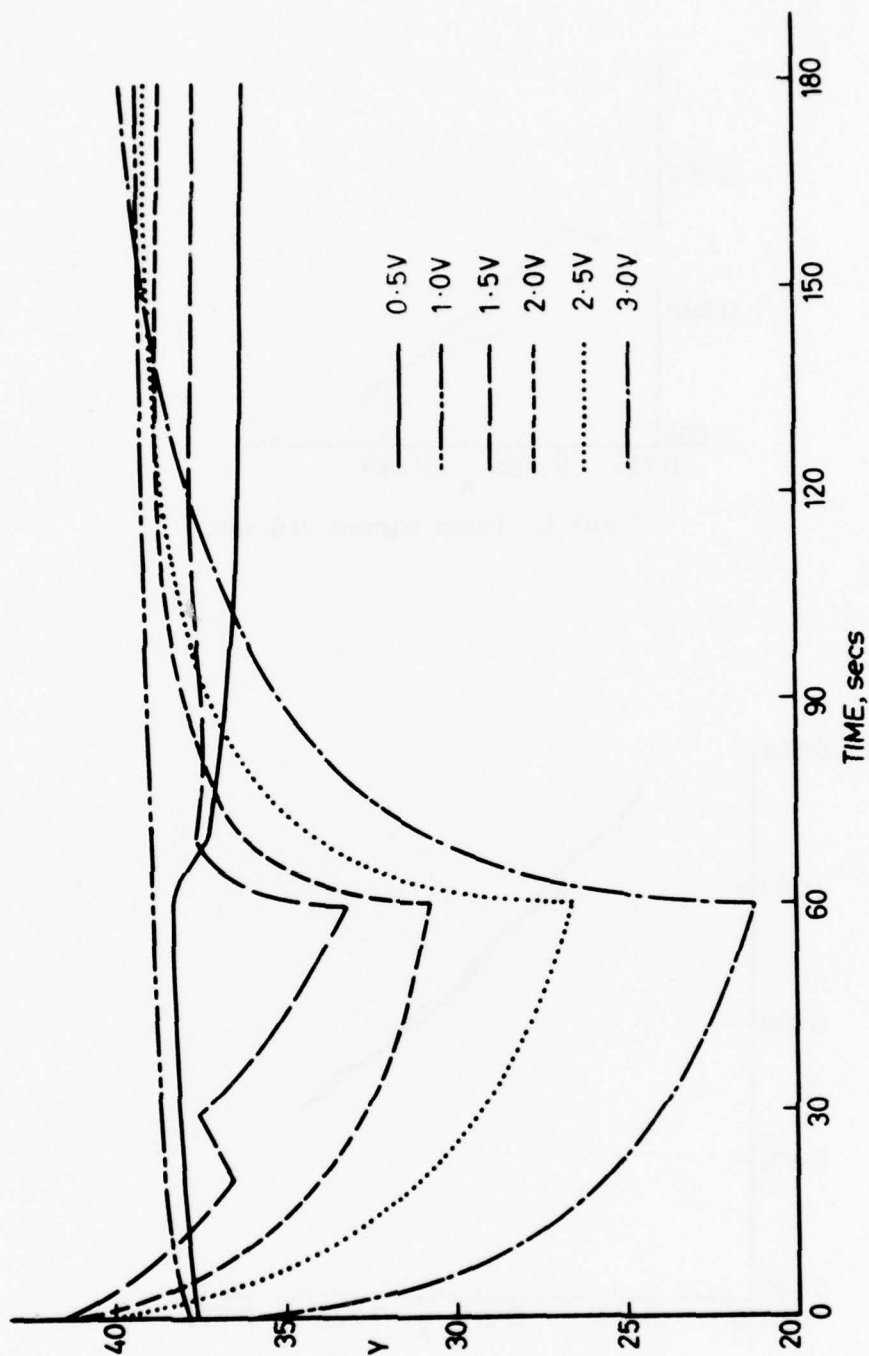


Figure 7. Lightness of yellow pigment as a function of time for several levels of applied voltage.

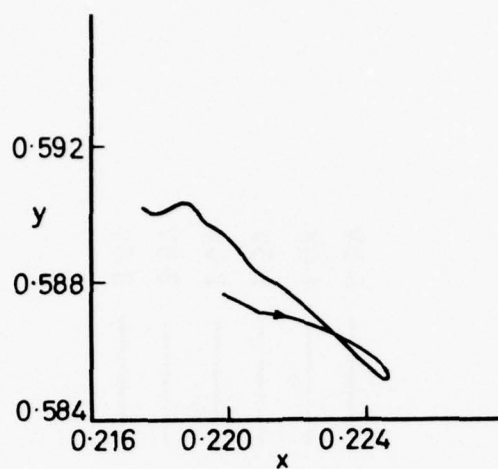


Figure 8. Green Pigment, 0.5 volt.

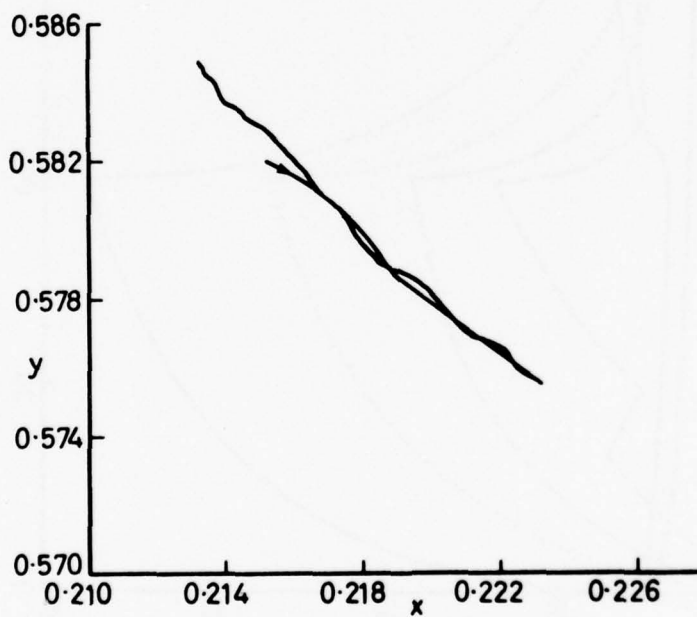


Figure 9. Green Pigment, 1.0 volt.

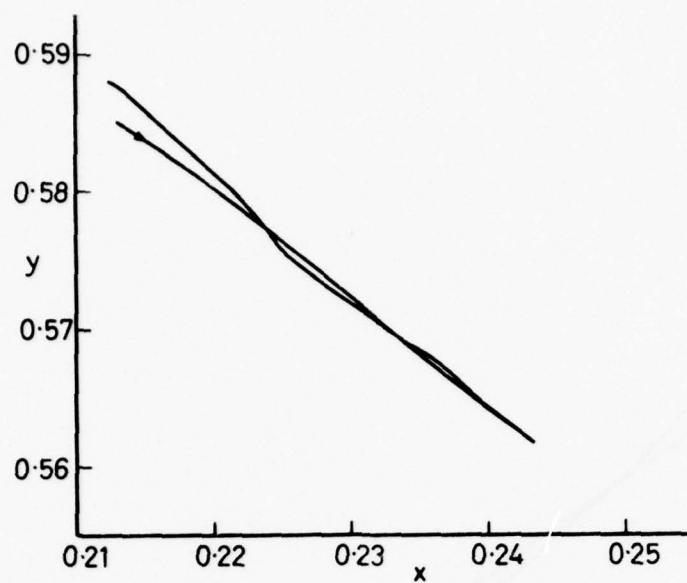


Figure 10. Green Pigment, 1.5 volts.

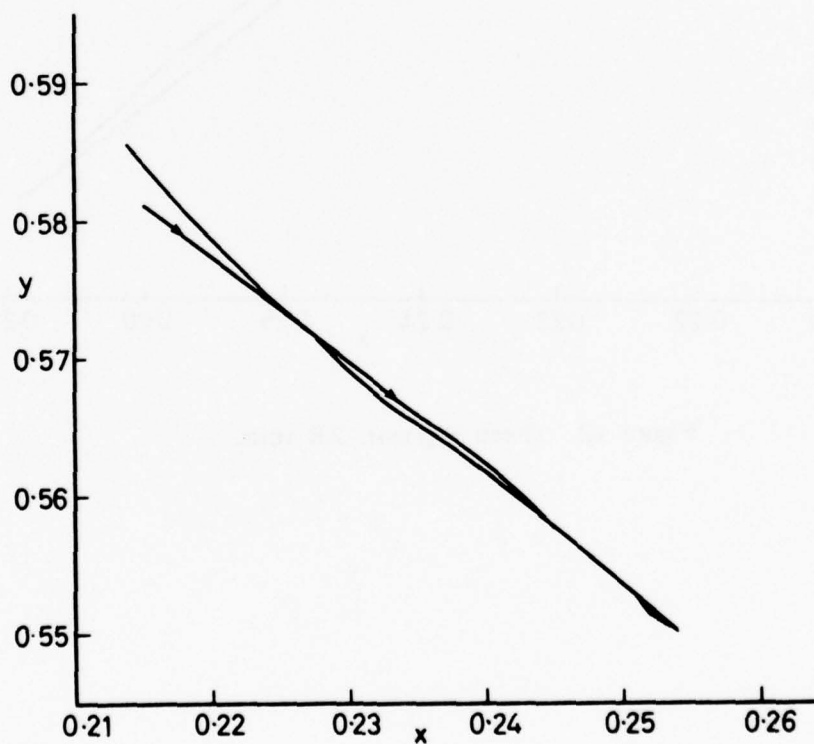


Figure 11. Green Pigment, 2.0 volts.

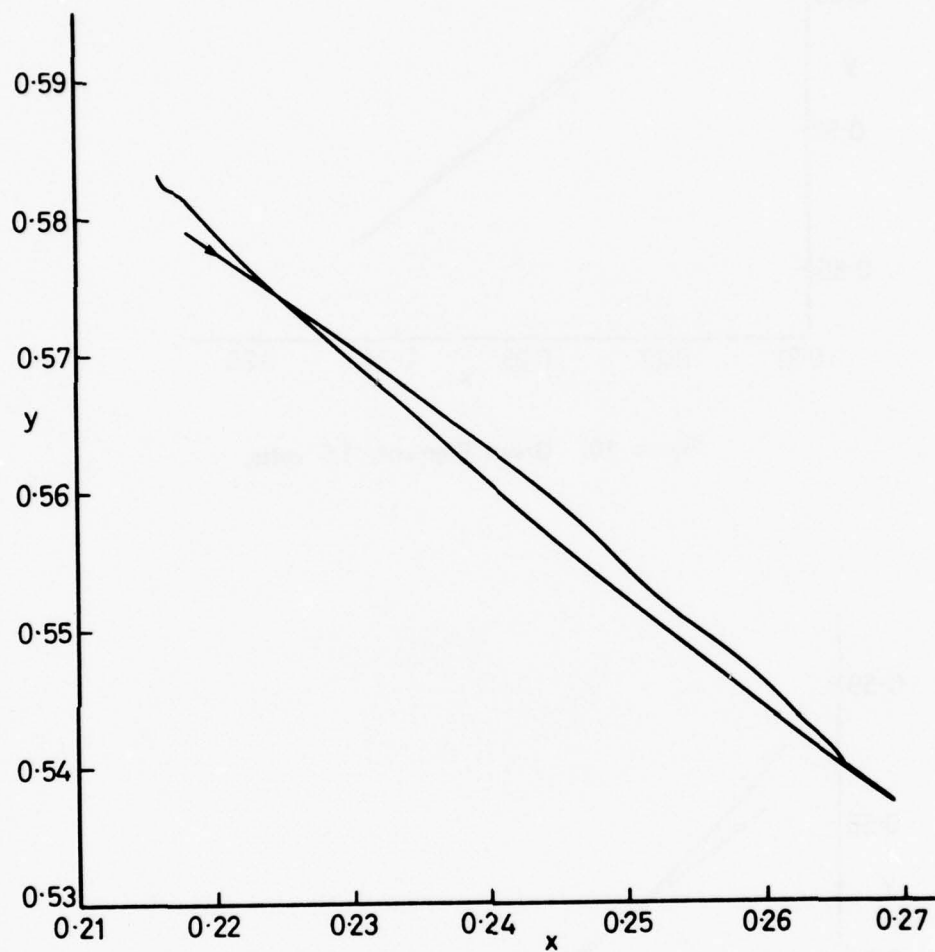


Figure 12. Green Pigment, 2.5 volts.

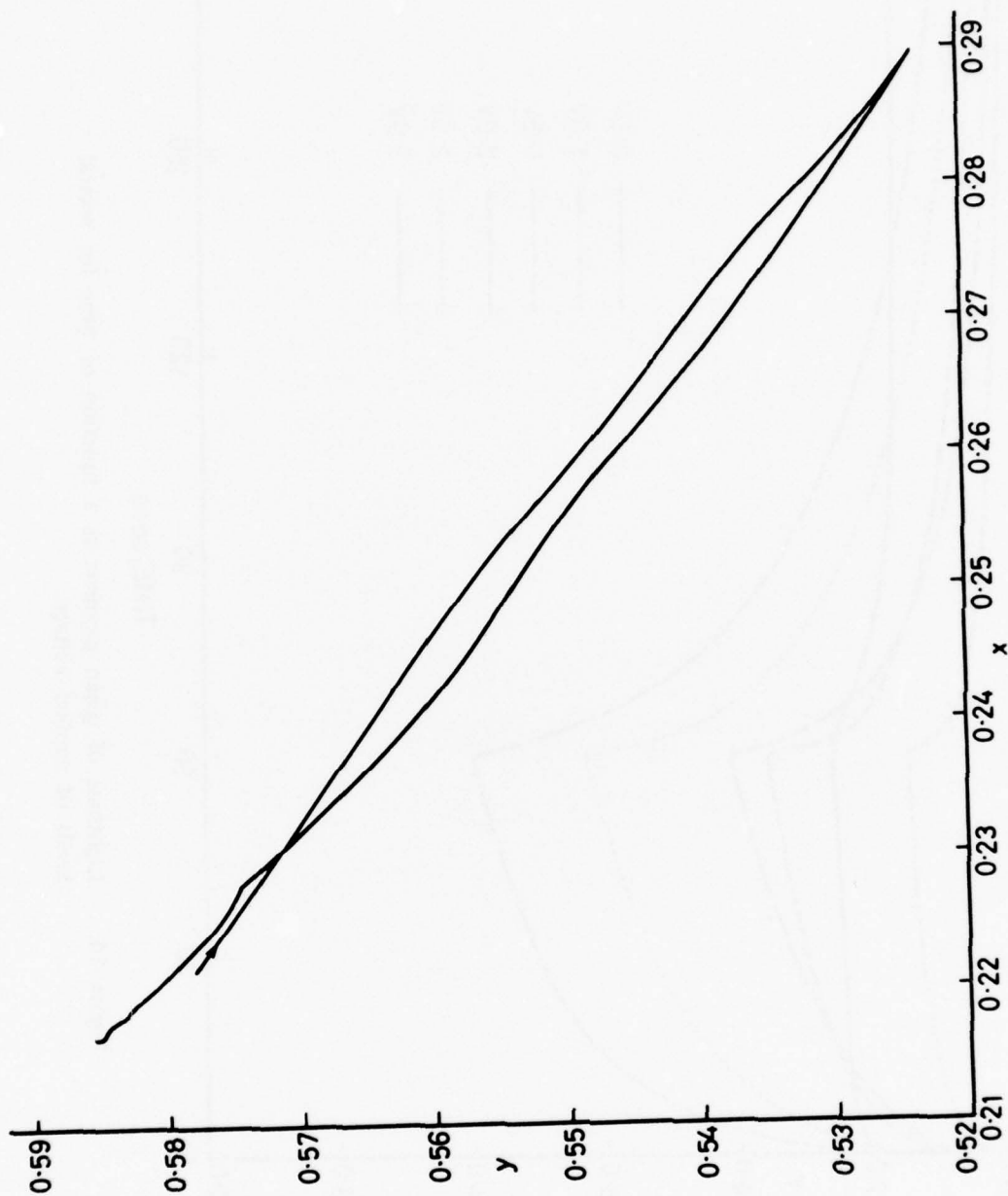


Figure 13. Green Pigment, 3.0 volts.

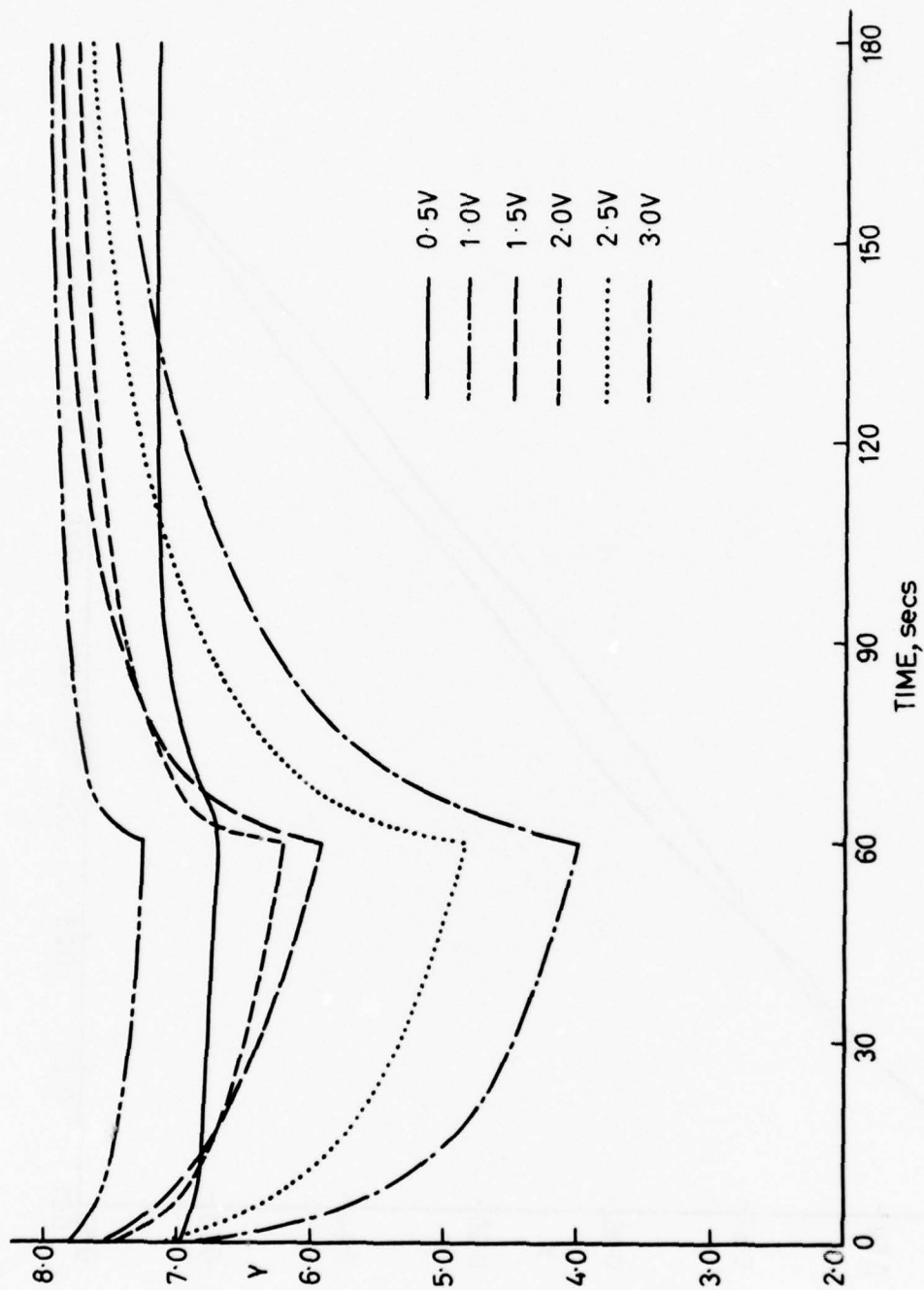


Figure 14. Lightness of green pigment as a function of time for several levels of applied voltage.

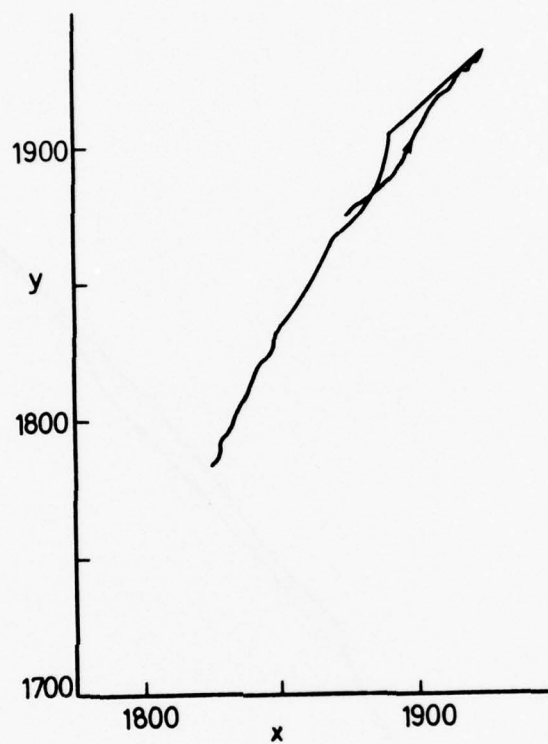


Figure 15. Blue Pigment, 0.5 volt.

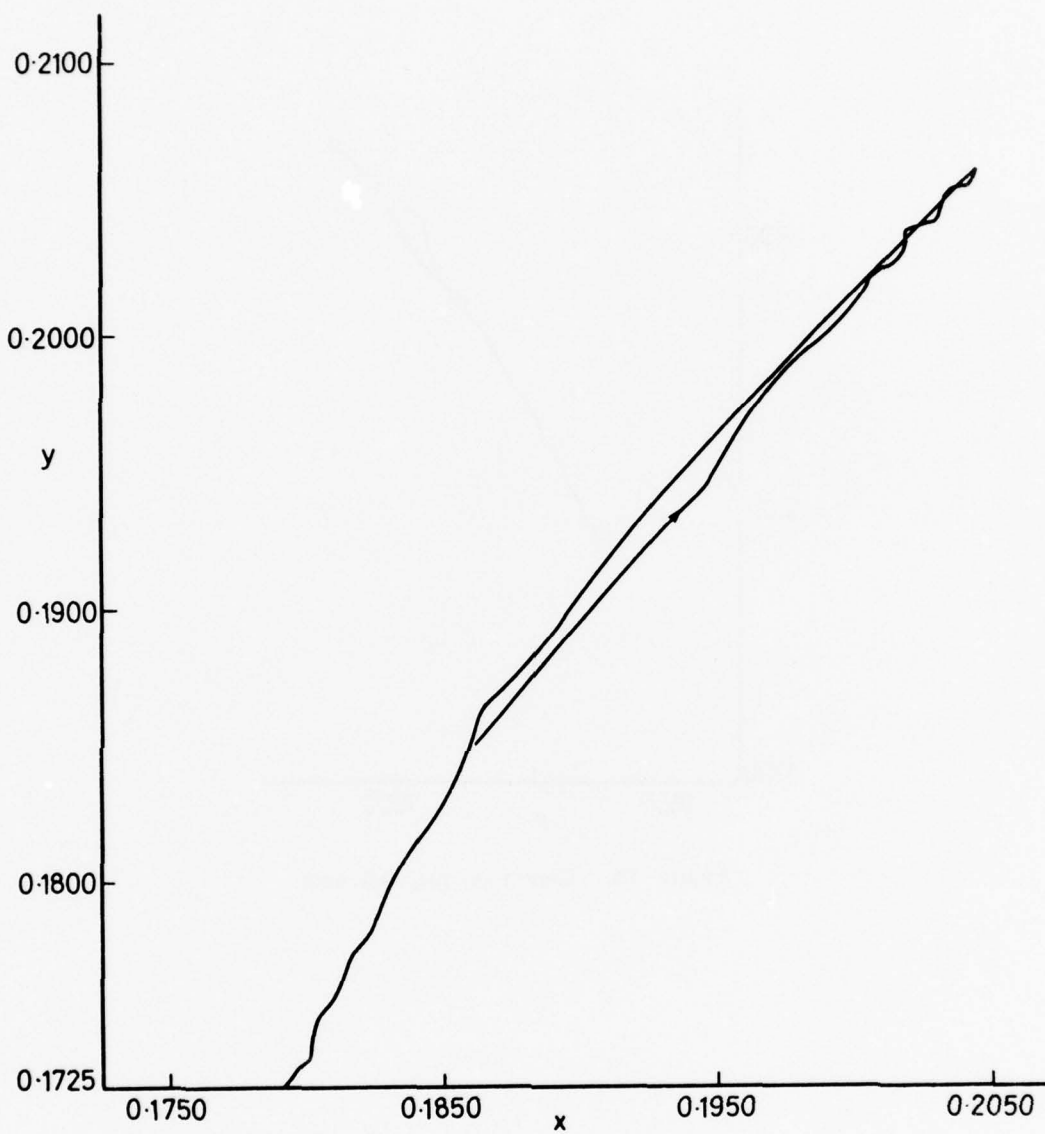


Figure 16. Blue Pigment, 1.0 volt.

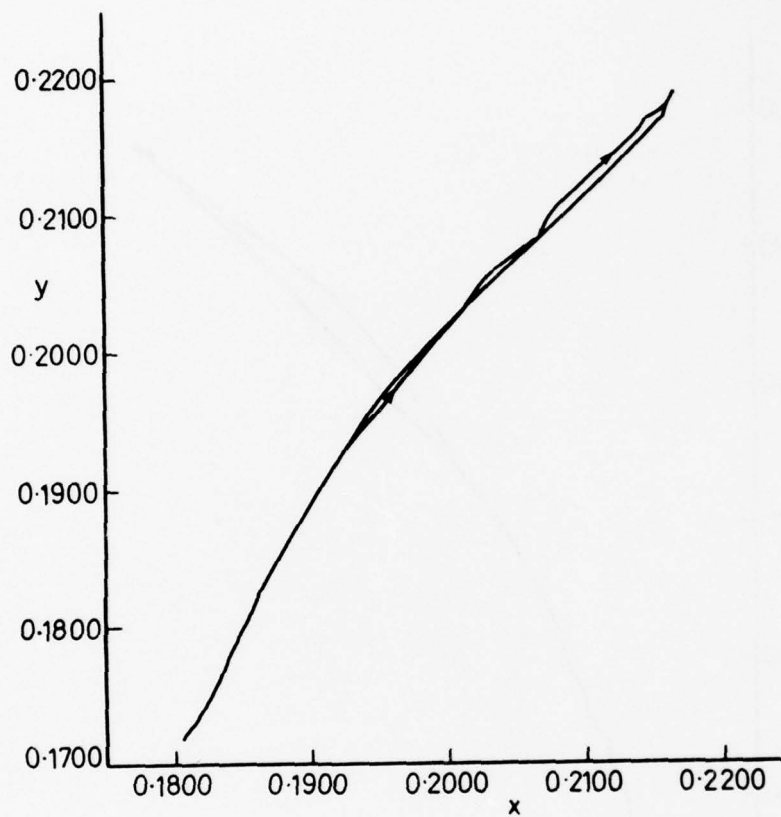


Figure 17. Blue Pigment, 1.5 volt.

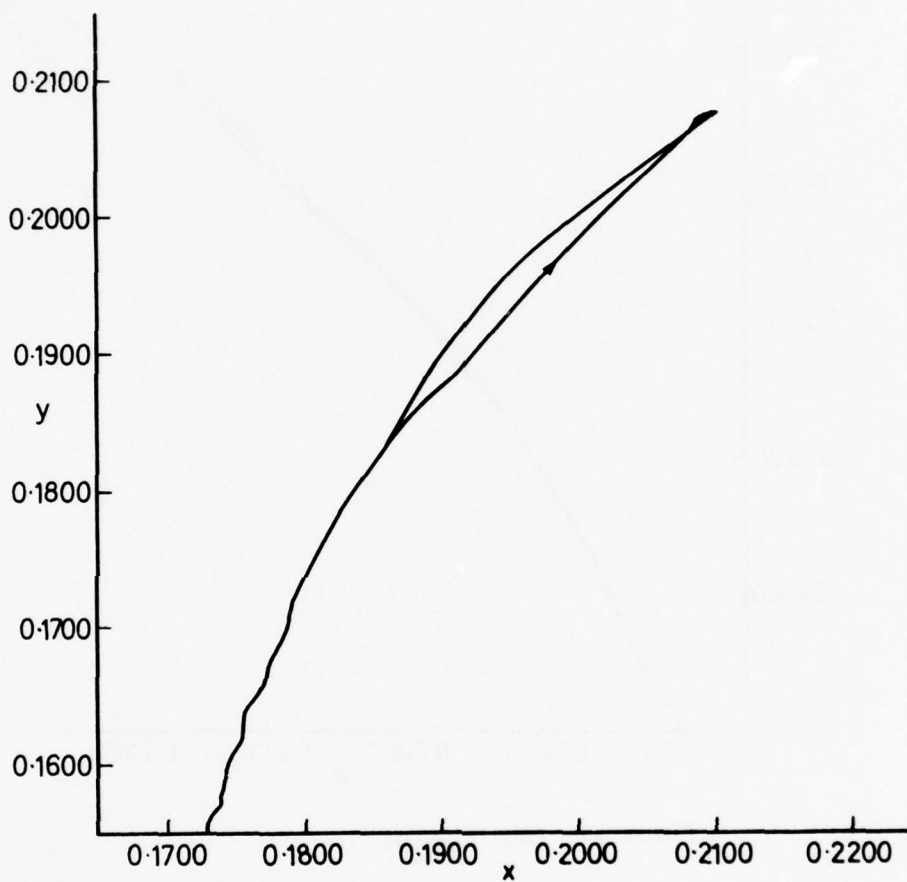


Figure 18. Blue Pigment, 2.0 volts.

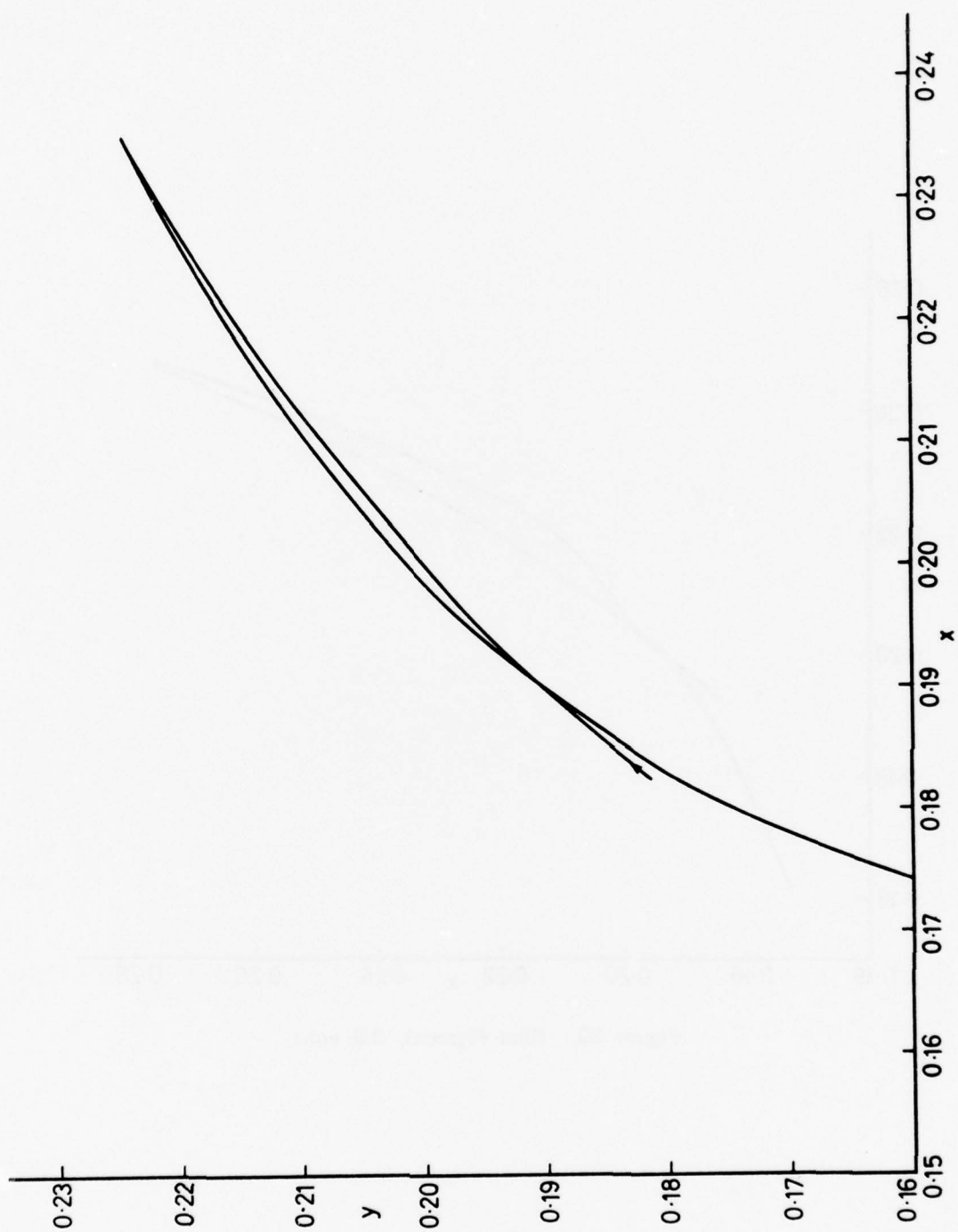


Figure 19. Blue Pigment, 2.5 volts.

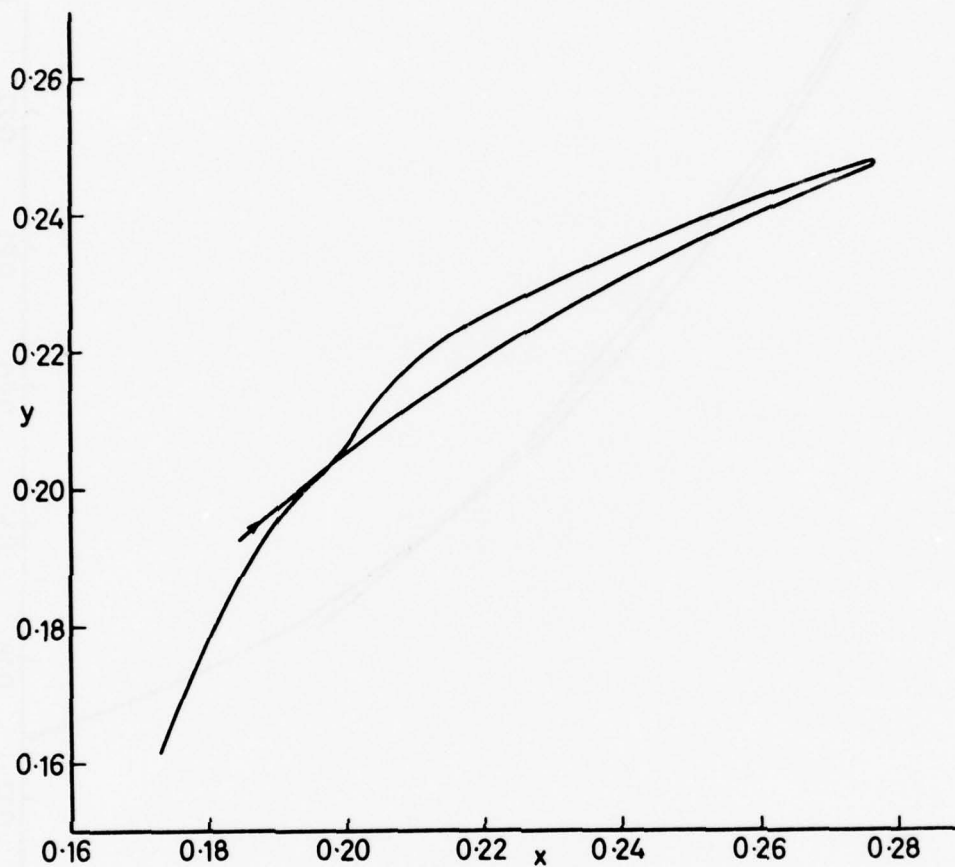


Figure 20. Blue Pigment, 3.0 volts.

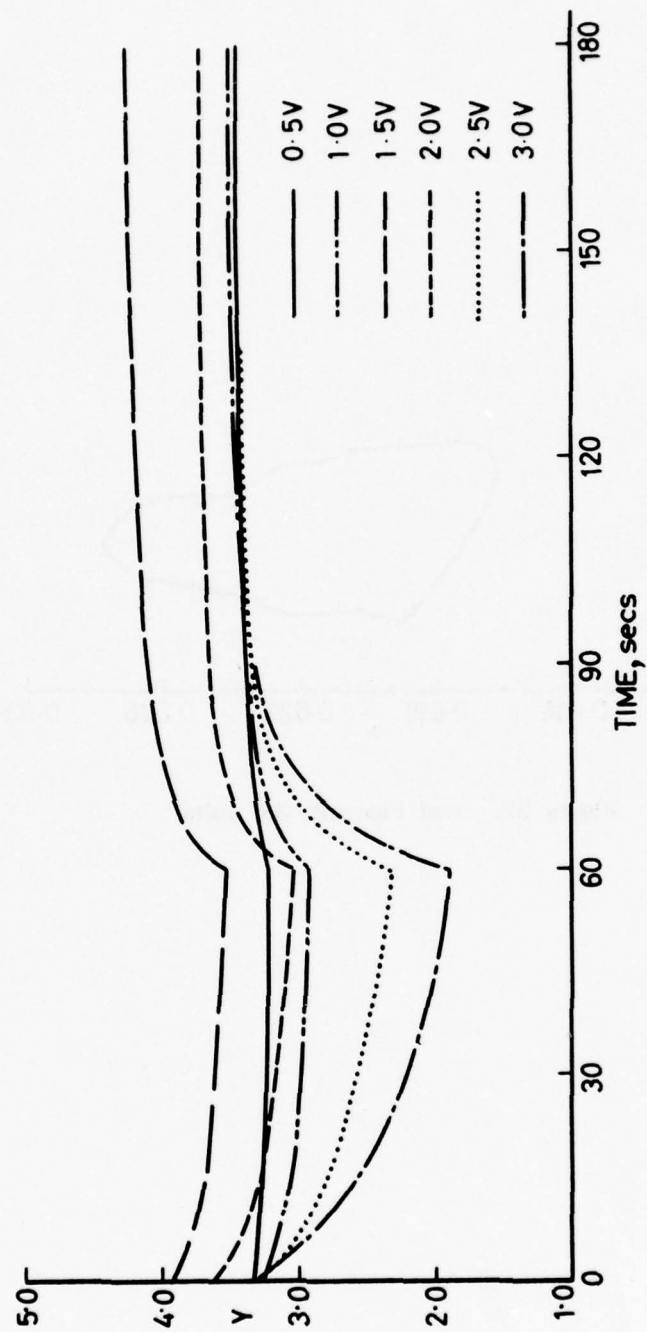


Figure 21. Lightness of blue pigment as a function of time for several levels of applied voltage.

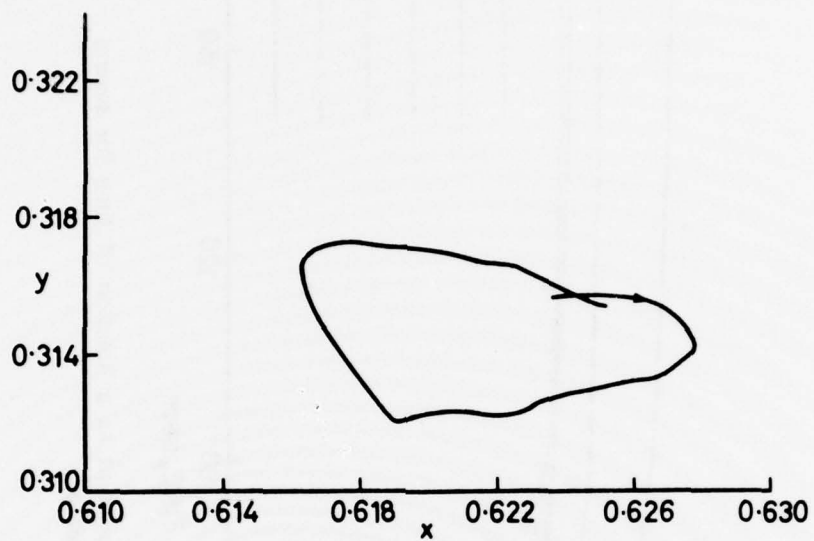


Figure 22. Red Pigment, 3.0 volts.

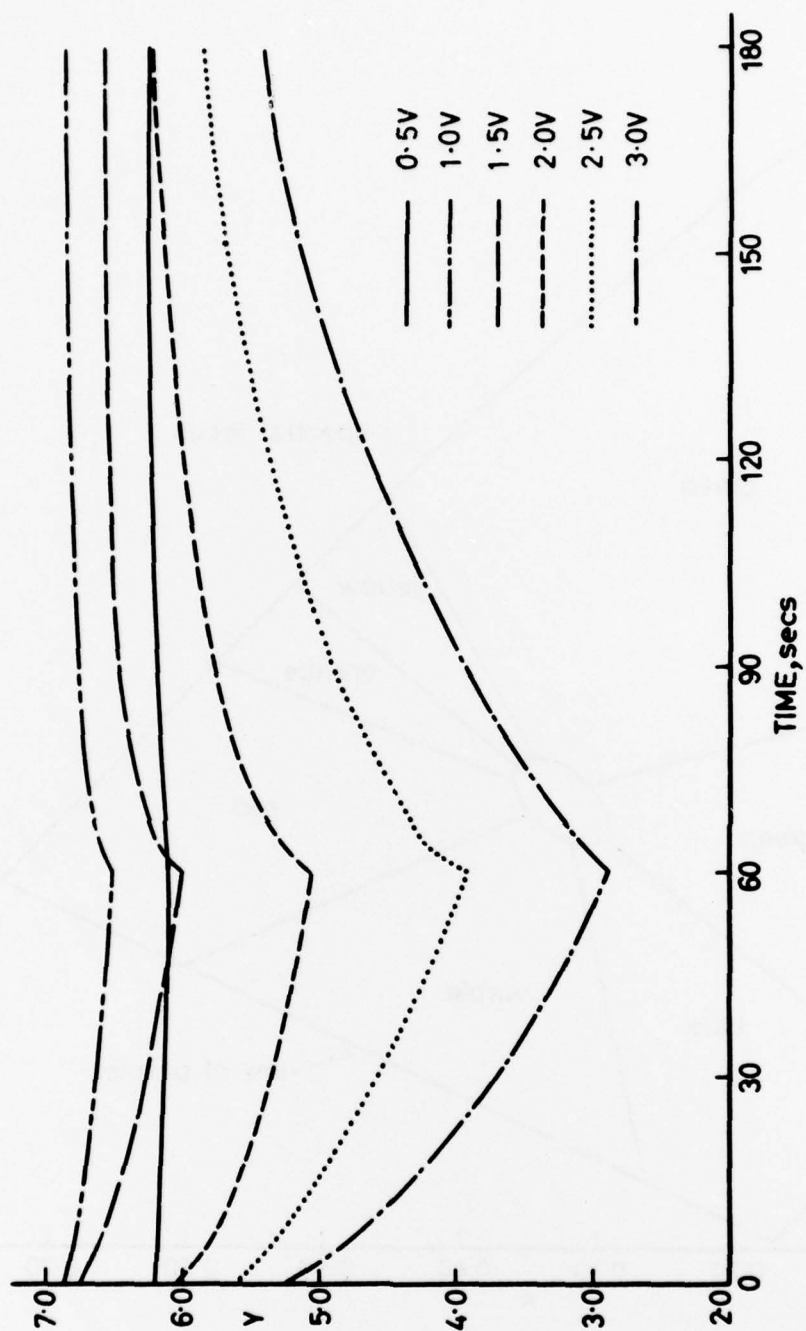


Figure 23. Lightness of red pigment as a function of time for several levels of applied voltage.

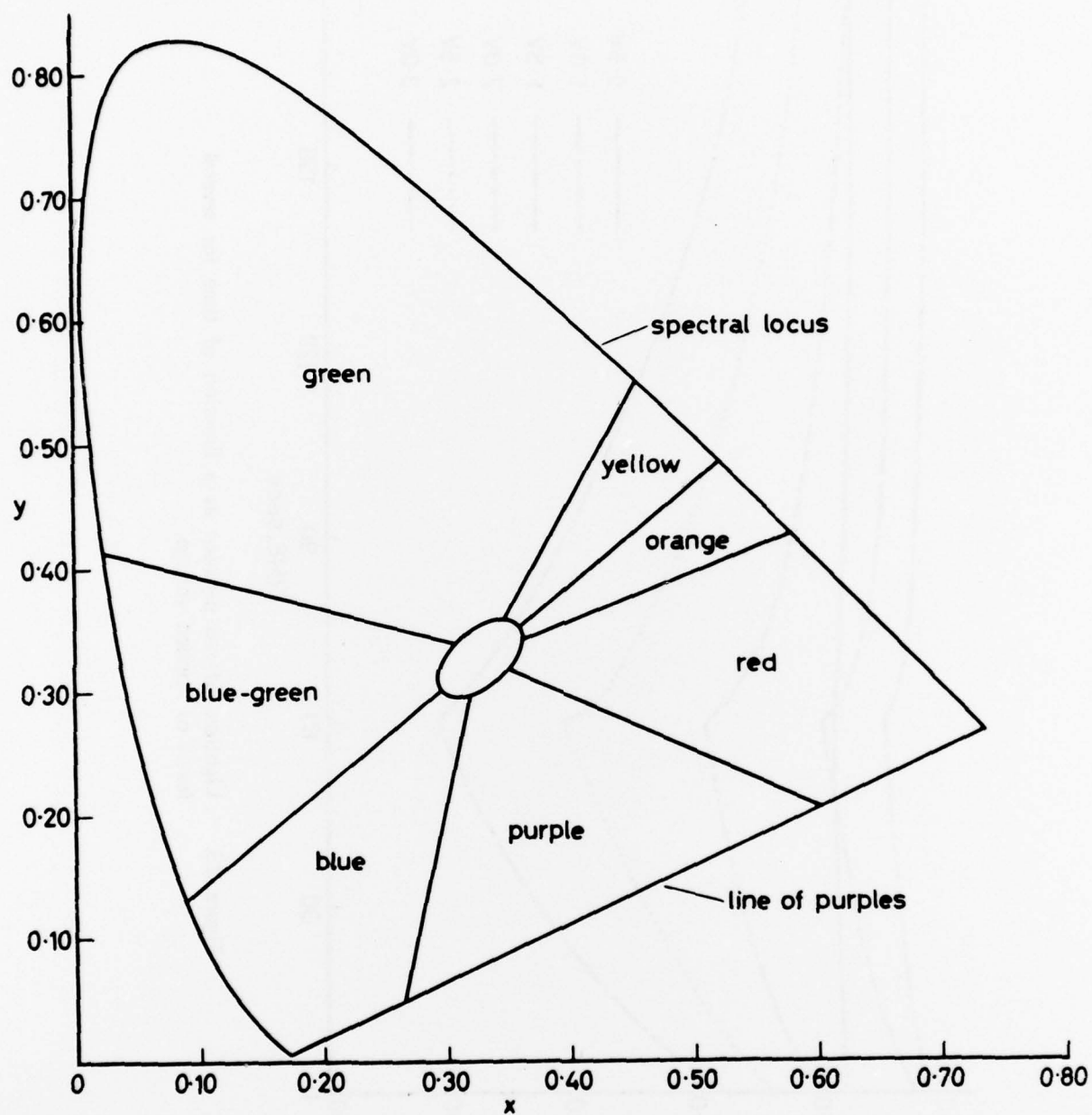


Figure 24. Color names referred to the CIE chromaticity diagram.

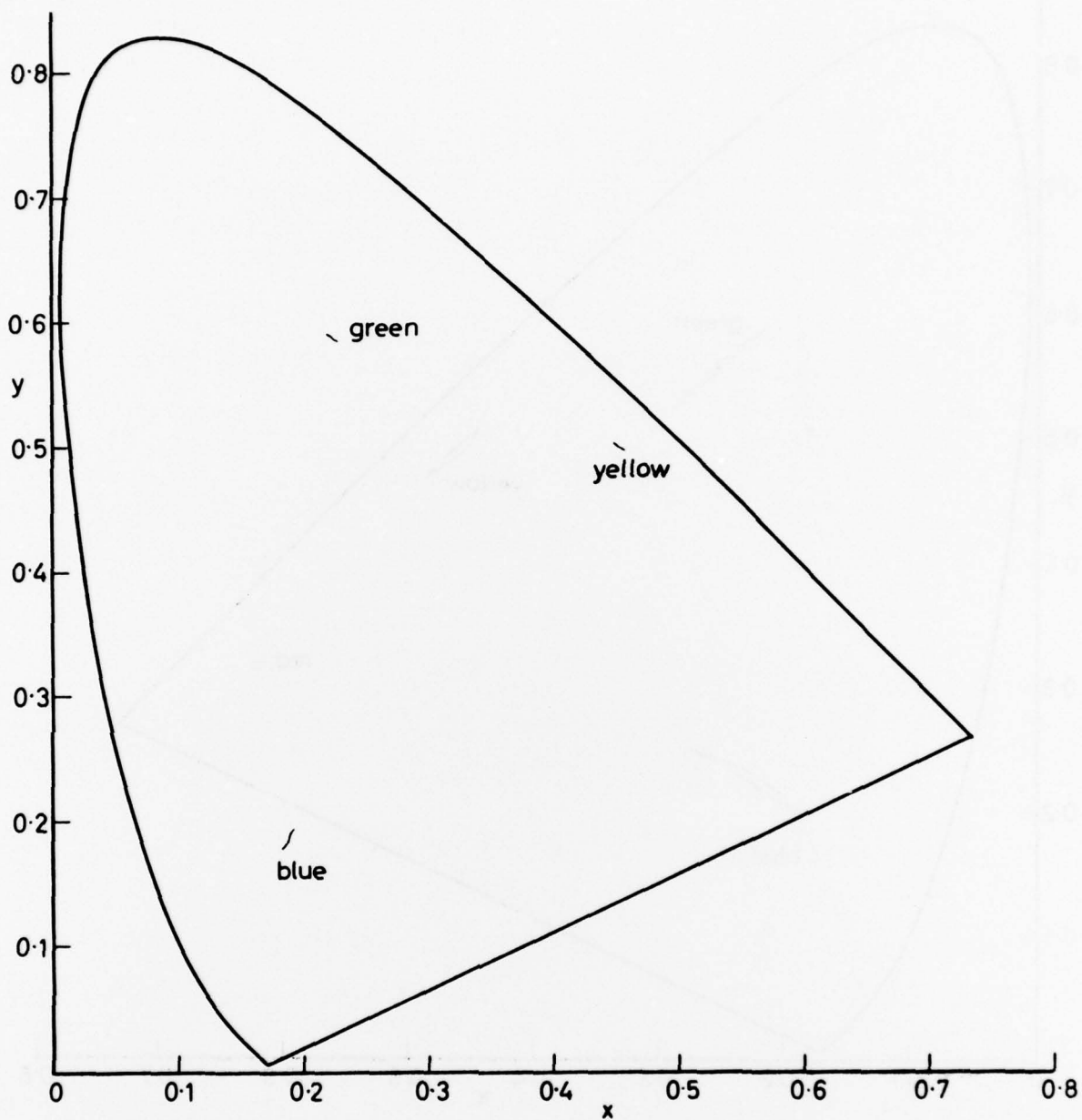


Figure 25. Changes in chromaticity produced at 0.5 volt for the yellow, green and blue pigments.

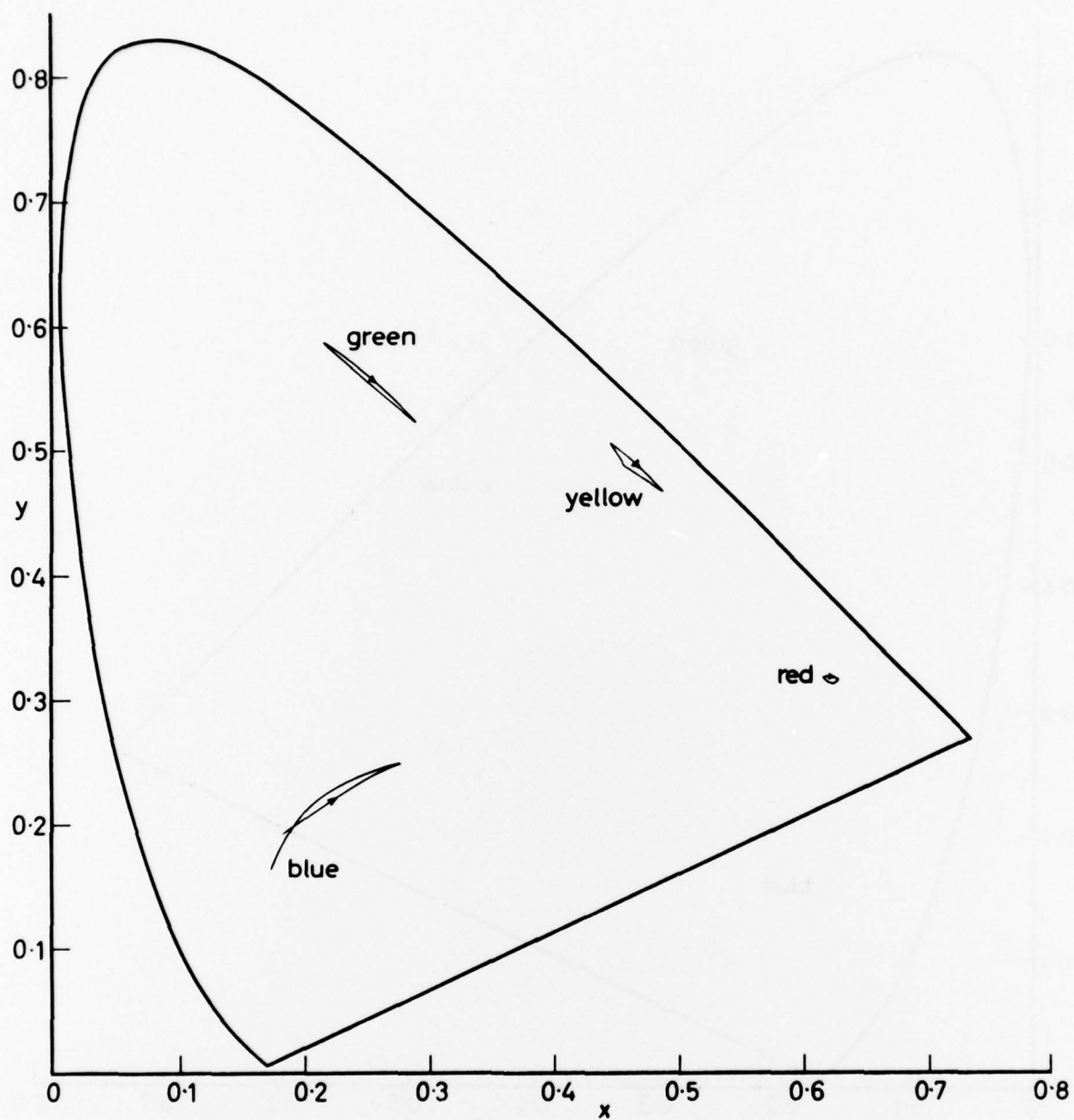


Figure 26. Changes in chromaticity produced at 3.0 volts for the yellow, green, blue, and red pigments.

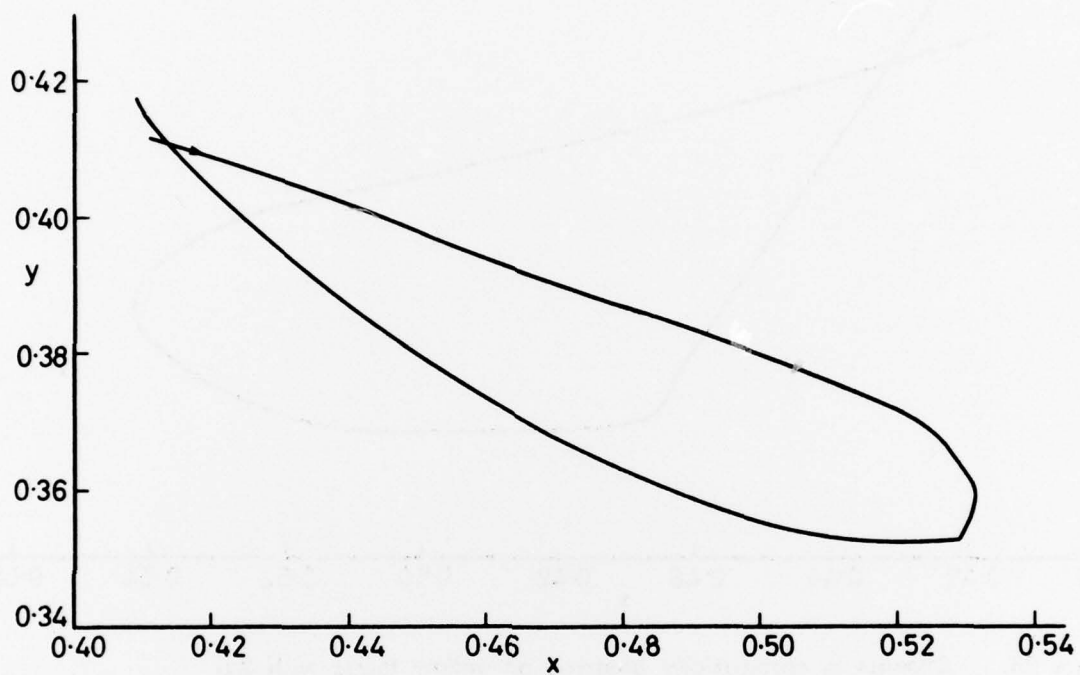


Figure 27. Changes in chromaticity observed on yellow fabric with 2.0 volts applied.

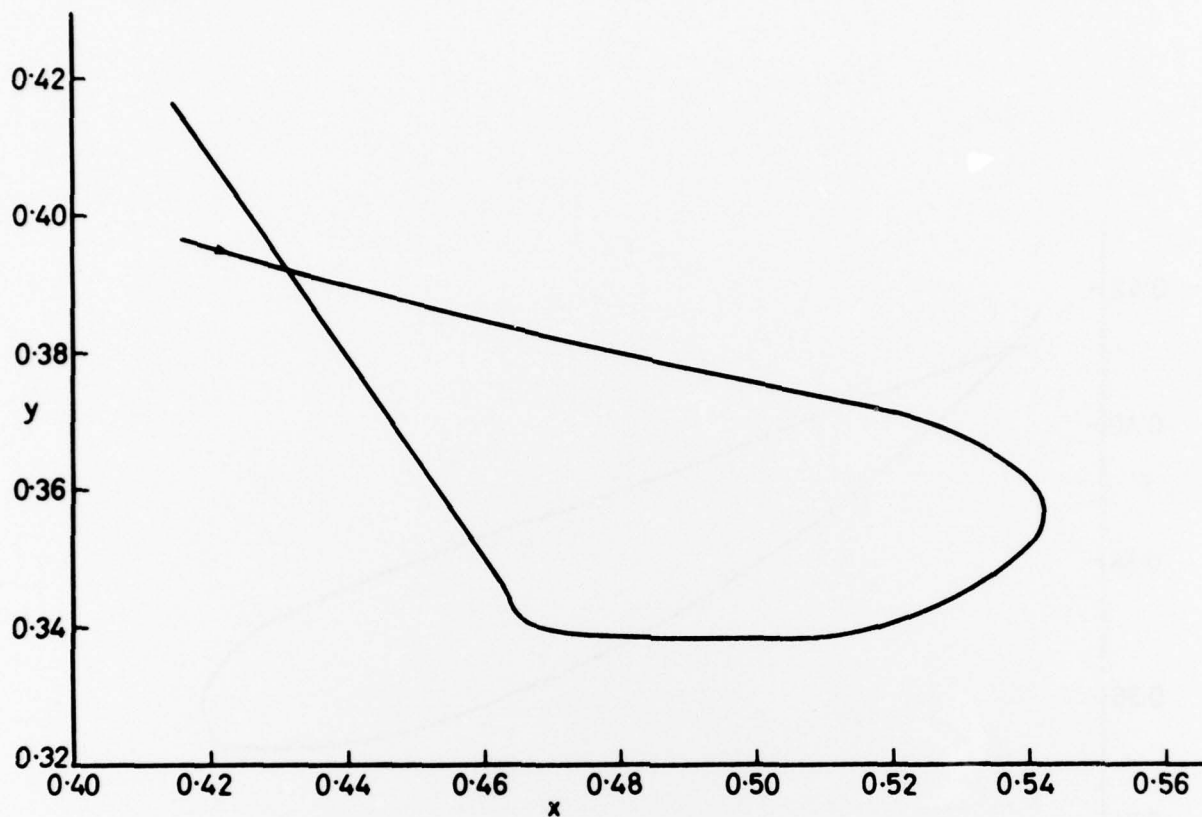


Figure 28. Changes in chromaticity observed on yellow fabric with 2.5 volts applied.

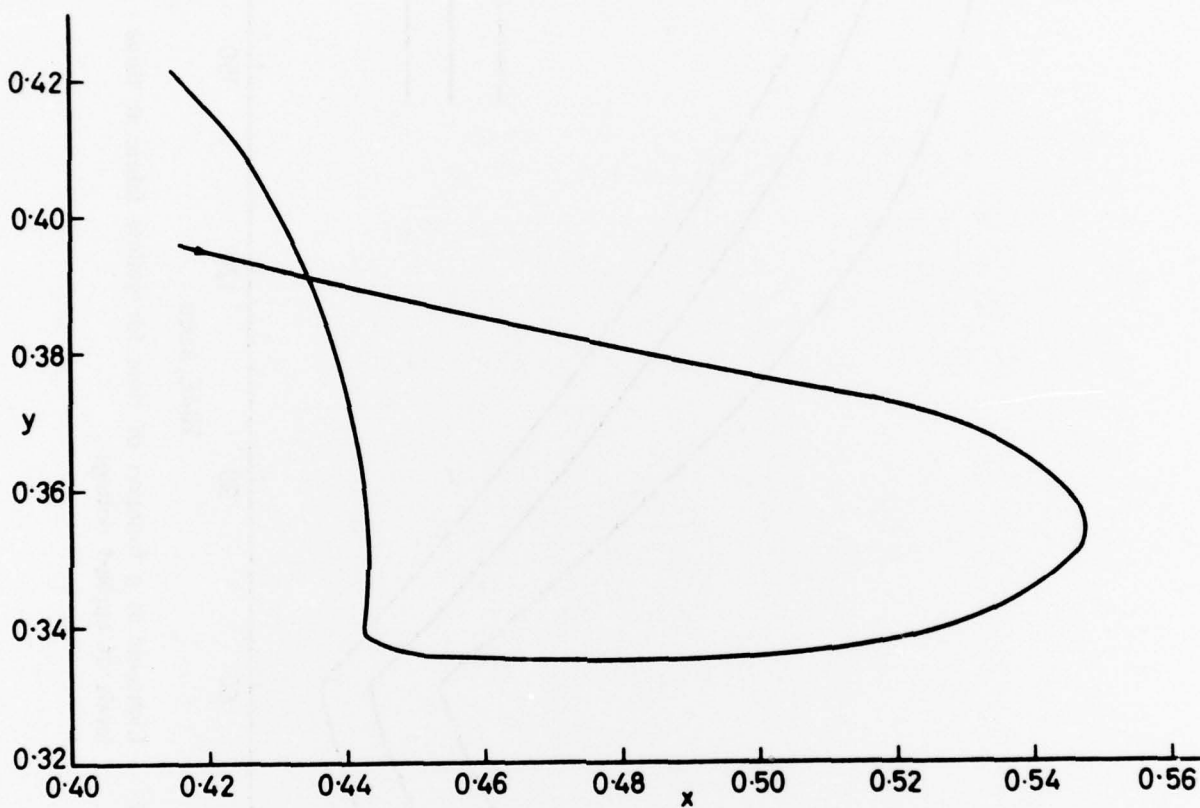


Figure 29. Changes in chromaticity observed on yellow fabric with 3.0 volts applied.



Figure 30. Lightness as a function of time for yellow fabric at three levels of applied voltage.

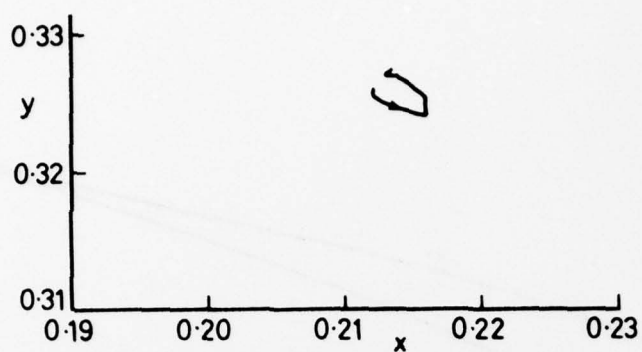


Figure 31. Chromaticity changes for Solway Green G 150 with 0.5 volts.

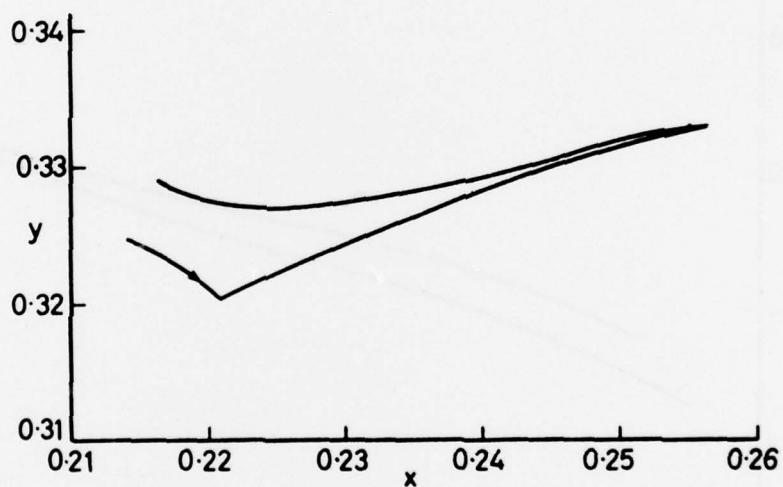


Figure 32. Chromaticity changes produced by 1.0 volt on Solway Green G 150.

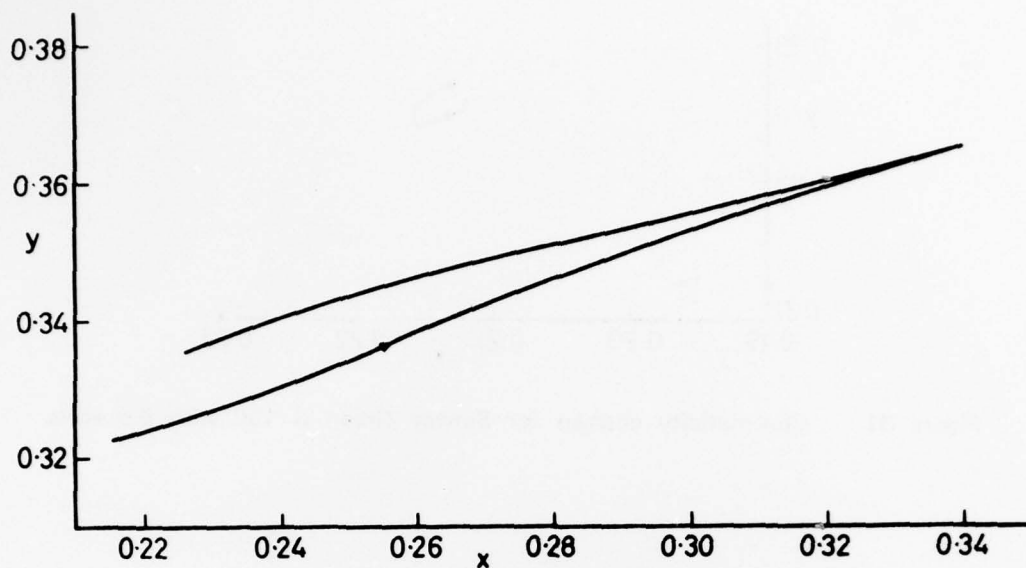


Figure 33. Chromaticity changes produced by 1.2 volts on Solway Green G 150.

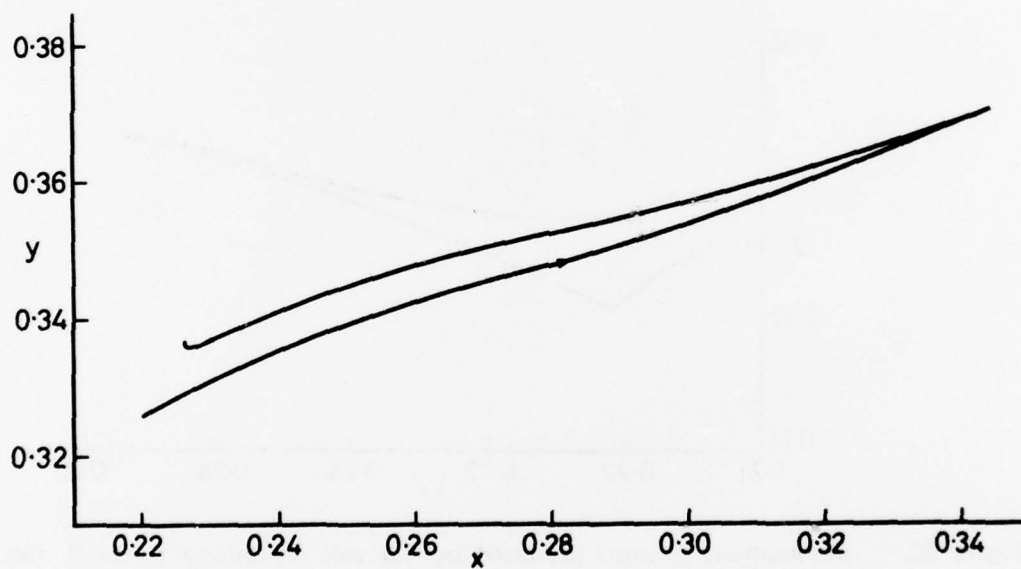


Figure 34. Chromaticity changes produced by 1.5 volts on Solway Green G 150.

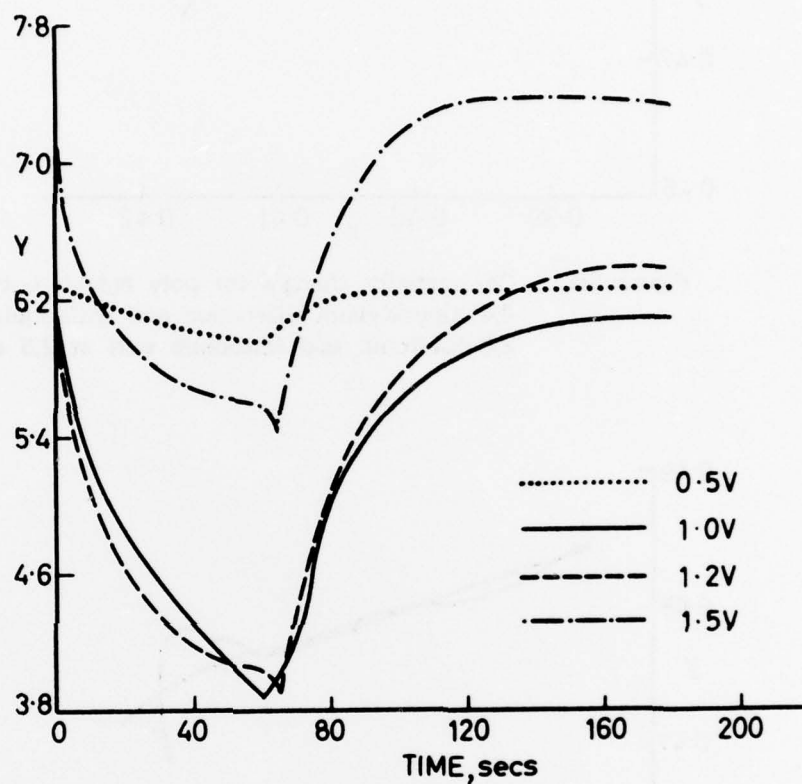


Figure 35. Lightness as a function of time for Solway Green G 150 for several levels of applied voltage.

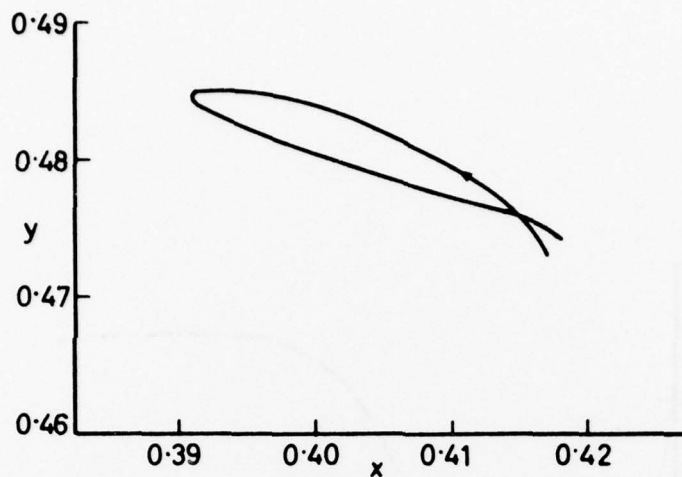


Figure 36. Chromaticity changes for poly N,N'-(n-butylene)-4,4'-bipyridylium dibromide and anthraquinone-2,6-disulfonic acid (disodium salt) at 2.5 volts.

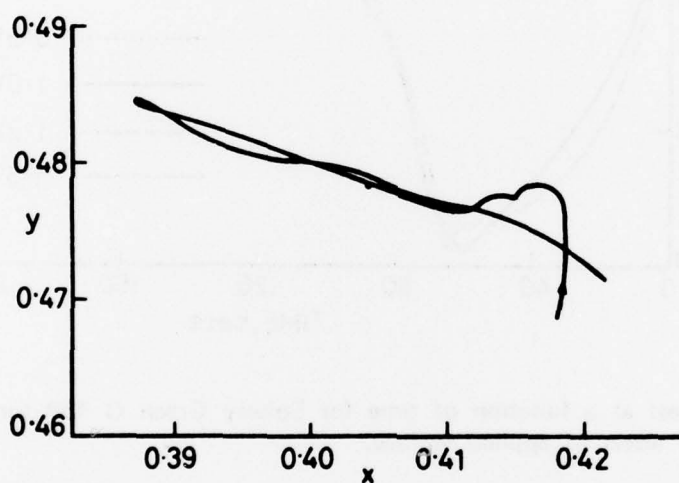


Figure 37. Chromaticity changes for poly N,N'-(n-butylene)-4,4'-bipyridylium dibromide and anthraquinone-2,6-disulfonic acid (disodium salt) at 3.0 volts.

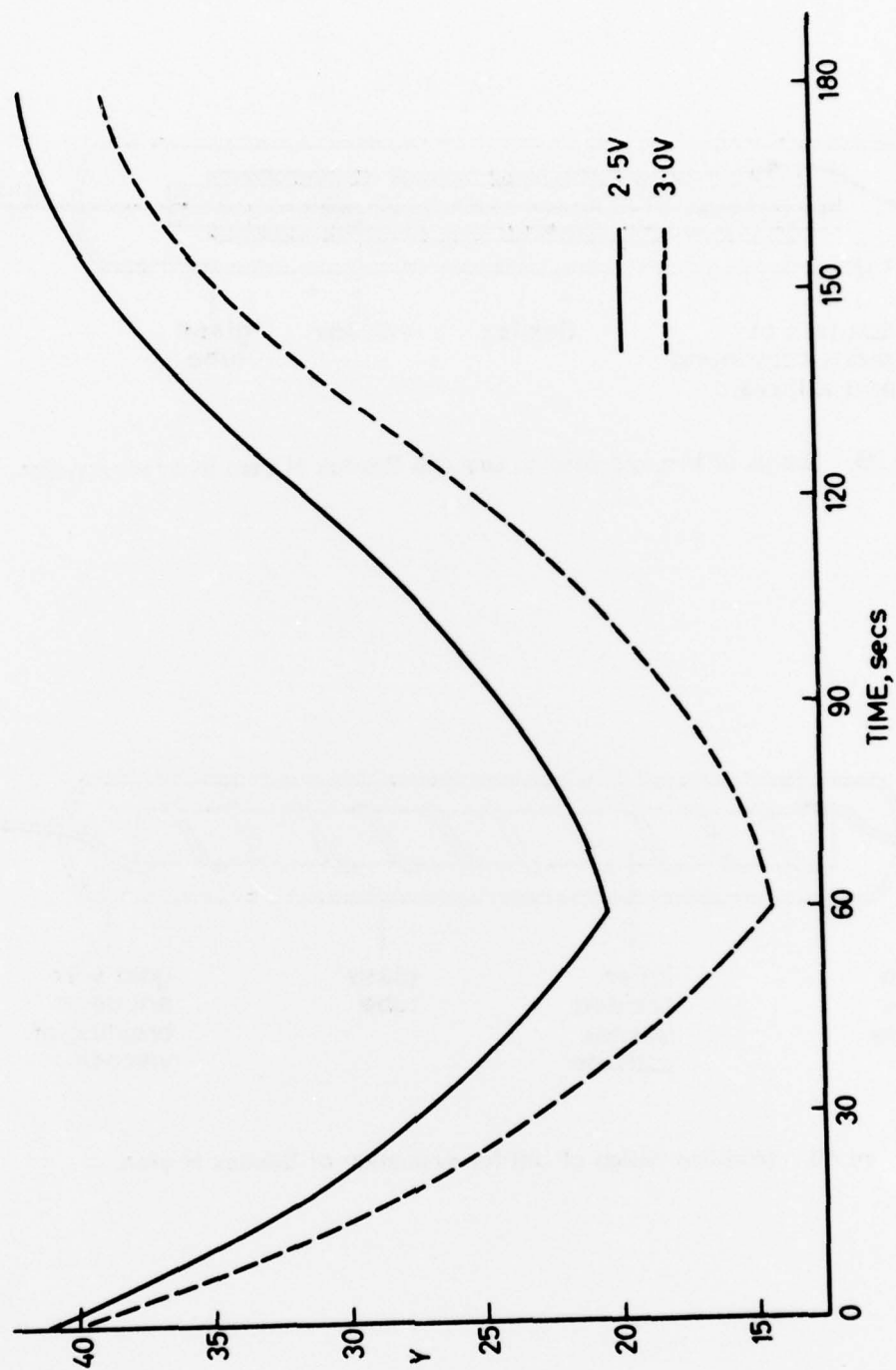


Figure 38. Color change for combination of Figure 36 as a function of time for the forward reaction.

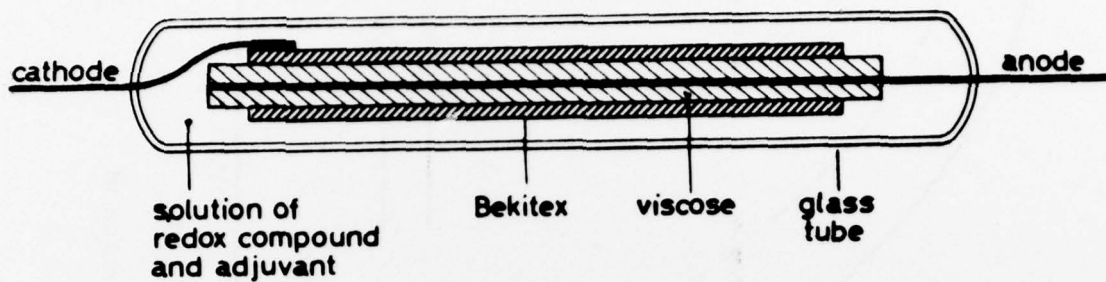


Figure 39. Design of first cell used to evaluate Bekitex H yarn in a redox system.

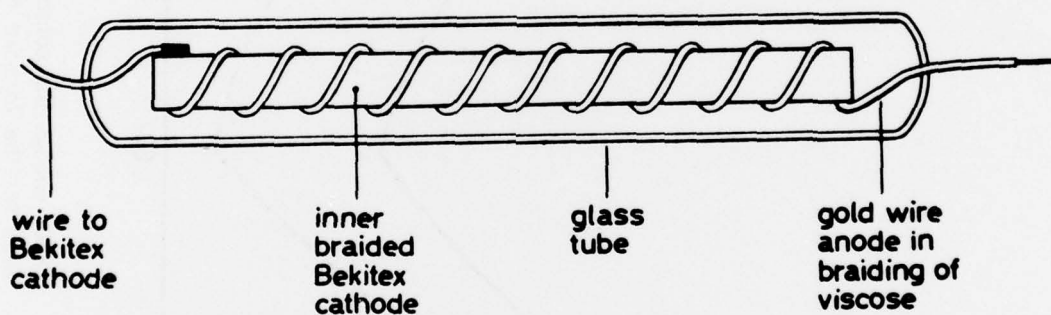


Figure 40. Modified design of cell for evaluation of Bekitex H yarn.